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(71) Applicants:
- JSR Corporation
  Tokyo 104-8410 (JP)
- BRIDGESTONE CORPORATION
  Tokyo 104-0031 (JP)

(72) Inventors:
- KONNO, Tomohisa
  Chuo-ku, Tokyo 104-8410 (JP)
- UDAGAWA, Yoshiyuki
  Chuo-ku, Tokyo 104-8410 (JP)
- TADAKI, Toshihiro c/o JSR CORPORATION
  Chuo-ku, Tokyo 104-8410 (JP)
- KONDO, Hajime
  Kodaira-shi, Tokyo 187-0031 (JP)
- YANAGISAWA, Kazuhiro
  Kodaira-shi, Tokyo 187-0031 (JP)

(74) Representative: Whalley, Kevin
MARKS & CLERK,
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) DIENE RUBBER/INORGANIC COMPOUND COMPOSITE AND METHOD FOR PRODUCING THE SAME AND RUBBER COMPOSITION

(57) The invention provides a diene-based rubber-inorganic compound composite material comprising a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM{\cdot}xSiO_y{\cdot}zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10), and a rubber composition comprising the composite material and a crosslinking agent.

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Description

TECHNICAL FIELD

[0001] This invention relates to a diene-based rubber-inorganic compound composite material and a method of producing the same and a rubber composition containing such a composite material, and more particularly to a rubber composition uniformly dispersing inorganic compound particles therein and capable of providing a rubber article having excellent wear resistance and tensile strength. Especially, the invention is utilized in not only a rubber for a tire such as a tire tread or the like but also various rubber articles such as belt, rubber roll, hose and so on.

BACKGROUND ART

[0002] Recently, there is proposed a method wherein an inorganic filler such as silica or the like is used or the inorganic filler and carbon black are used together as a reinforcing agent in a rubber composition for a tire. A tire tread made of a rubber composition containing the inorganic filler or the inorganic filler and carbon black has a low rolling resistance and an excellent steering stability represented by a wet skid resistance. However, there is a problem that wear resistance, tensile strength and so on of a vulcanized rubber are poor.

[0003] Especially, when silica is applied as an inorganic filler, in order to enhance an affinity with a conjugated diene rubber, it is examined to use a conjugated diene rubber introduced with a functional group having an affinity with silica up to now. For instance, there are proposed a hydroxyl group-introduced conjugated diene rubber (WO96/23027), an alkoxysilyl group-introduced conjugated diene rubber (JP-A-9-208623), and an alkoxysilyl group and amino group or hydroxyl group-introduced conjugated diene rubber (JP-A-9-208633). However, the most kind of the conjugated diene rubbers introduced with these functional groups are strong in the interaction with silica, so that they have problems that when being mixed with silica, a poor dispersion of silica is caused, and heat generation in processing is large, and the processability is poor and so on.

[0004] Particularly, when the conjugated diene rubber is milled with the inorganic filler in a dry process to make a rubber composition, the inorganic filler is not sufficiently dispersed into the rubber and hence there is a problem that sufficiently improved properties such as wear resistance and the like are not obtained.

[0005] On the other hand, JP-A-59-49247 and so on propose a method wherein carbon black is compounded and dispersed in an aqueous dispersion containing rubber such as a latex or the like dispersed therein and then coagulated to prepare a carbon black master batch in order to simplify a milling step with carbon black as a reinforcing agent or improve dispersion into rubber. And also, it is attempted to prepare a master batch of silica according to this method, but it is not practically easy to obtain a uniform master batch because silica having a large hydrophilic nature is hardly agglomerated and only the rubber component is preferentially agglomerated and precipitated.

[0006] Further, it is known to obtain a rubber composition by applying only powder of aluminum hydroxide as a reinforcing filler for rubber instead of silica or carbon black and milling with rubber component in a dry process (see a column of Prior Art in JP-A-2000-204197). However, such a rubber composition has a problem that the wear resistance is poor.

[0007] As an improvement of the rubber composition, there are also known (1) application of a combination of silica and/or carbon black and aluminum hydroxide (JP-A-2000-204197, JP-A-2000-302914), and (2) application of a combination of silica and aluminum hydroxide, magnesium hydroxide and so on (JP-A-11-181155). Even in these cases, however, powders of starting materials are milled in a dry process to prepare a rubber composition, so that there is a problem that sufficient wear resistance and tensile strength are not necessarily obtained because aluminum hydroxide and so on are not sufficiently dispersed.

DISCLOSURE OF THE INVENTION

[0008] The invention solves the aforementioned problems of the conventional techniques and is to provide a diene-based rubber-inorganic compound composite material obtained through a step of mixing an aqueous dispersion containing a diene-based rubber dispersed therein with an aqueous dispersion of an inorganic compound such as silica, aluminum hydroxide, kaolin or the like, an aqueous solution of an inorganic salt or the like, and a rubber composition containing such a composite material and uniformly dispersed the inorganic compound and capable of producing a rubber article having excellent wear resistance and tensile strength.

[0009] A first aspect of the invention lies in a diene-based rubber-inorganic compound composite material (hereinafter referred to as a composite material simply) comprising a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \quad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10), and produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous dispersion of the inorganic compound.

[0010] A second aspect of the invention lies in a diene-based rubber-inorganic compound composite material comprising a diene-based rubber and an inorganic compound represented by the above formula (I) and produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous solution of an inorganic salt capable of forming the inorganic compound represented by the formula (I).

[0011] A third aspect of the invention lies in a diene-based rubber-inorganic compound composite material comprising a diene-based rubber and an inorganic compound represented by the above formula (I) and produced through a step of mixing an aqueous dispersion of the diene-based rubber with a solution of an organic metal compound capable of forming the inorganic compound represented by the formula (I).

[0012] A fourth aspect of the invention lies in a method of producing a diene-based rubber-inorganic compound composite material which comprises mixing an aqueous dispersion of a diene-based rubber with an aqueous dispersion of an inorganic compound.

[0013] A fifth aspect of the invention lies in a method of producing a diene-based rubber-inorganic compound composite material which comprises a step of mixing an aqueous dispersion of a diene-based rubber with an aqueous dispersion of at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \quad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10).

[0014] A sixth aspect of the invention lies in a method of producing a diene-based rubber-inorganic compound composite material which comprises a step of mixing an aqueous dispersion of a diene-based rubber with an aqueous solution of an inorganic salt capable of forming the inorganic compound represented by the formula (I).

[0015] A seventh aspect of the invention lies in a method of producing a diene-based rubber-inorganic compound composite material which comprises a step of mixing an aqueous dispersion of a diene-based rubber with a solution of an organic metal compound capable of forming the inorganic compound represented by the formula (I).

[0016] An eighth aspect of the invention lies in a rubber composition comprising a diene-based rubber-inorganic compound composite material, which comprises a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \quad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10) and is produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous dispersion of the inorganic compound, and a crosslinking agent.

[0017] A ninth aspect of the invention lies in a rubber composition comprising a diene-based rubber-inorganic compound composite material, which comprises a diene-based rubber and an inorganic compound represented by the formula (I) and is produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous solution of an inorganic salt capable of forming the inorganic compound represented by the formula (I), and a crosslinking agent.

[0018] A tenth aspect of the invention lies in a rubber composition comprising a diene-based rubber-inorganic compound composite material, which comprises a diene-based rubber and an inorganic compound represented by the formula (I) and is produced through a step of mixing an aqueous dispersion of the diene-based rubber with a solution of an organic metal compound capable of forming the inorganic compound represented by the formula (I), and a crosslinking agent.

[0019] The "diene-based rubber" used in the invention is a rubber having a conjugated diene-based monomer unit as a monomer unit constituting rubber and is not particularly limited, but includes natural rubber, butadiene rubber,

isoprene rubber, styrene-butadiene copolymer rubber, butadiene-isoprene copolymer rubber, butadiene-styrene-isoprene copolymer rubber, acrylonitrile-butadiene copolymer rubber, acrylonitrile-styrene-butadiene copolymer rubber, chloroprene rubber and so on. Among these rubbers, a rubber obtained by polymerizing a conjugated diene monomer and, if necessary, an aromatic vinyl monomer, an olefinic unsaturated nitrile monomer through an emulsion polymerization is particularly preferable, which can include an emulsion-polymerized butadiene rubber, an emulsion-polymerized styrene-butadiene copolymer rubber, an emulsion-polymerized acrylonitrile-butadiene copolymer rubber and an emulsion-polymerized acrylonitrile-styrene-butadiene copolymer rubber. And also, the diene-based rubber may be an oil-extended type or a non-oil extended type.

[0020] As the "aqueous dispersion of diene-based rubber" used in the invention, a diene-based rubber latex obtained by the emulsion polymerization is favorable. This diene-based rubber latex is a dispersion of diene-based rubber particles into an aqueous medium and includes a natural rubber latex, an emulsion obtained by again emulsifying a diene-based synthetic rubber, a diene-based synthetic rubber emulsion produced by polymerizing in an aqueous medium, a dispersion of a diene-based synthetic rubber and so on. These latexes may be used alone or in a combination of two or more, irrespectively of the kind of the diene-based rubber or the kind of the aqueous dispersion.

[0021] As the conjugated diene monomer (hereinafter referred to as "conjugated diene"), mention may be made of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-chloro-1,3-butadiene, 1,3-pentadiene, isoprene and the like. Among them, 1,3-butadiene and isoprene are favorable, and 1,3-butadiene is more preferable. These conjugated dienes may be used alone or in a combination of two or more.

[0022] As the aromatic vinyl monomer are used aromatic vinyl compounds having no polar group, which include, for example, styrene, α-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2,4-diisopropylstyrene, 2,4-dimethylstyrene, 4-t-butylstyrene, 5-t-butyl-2-methylstyrene, monochlorostyrene, dichlorostyrene, monofluorostyrene and so on. Among them, styrene is favorable. The aromatic vinyl compounds may be used alone or in a combination of two or more.

[0023] As the olefinic unsaturated nitrile monomer, mention may be made of (meth)acrylonitrile, vinylidene cyanide and so on. These monomers having nitrile group may be used alone or in a combination of two or more.

[0024] And also, the diene-based rubber may be a diene-based rubber having a polar group of a heteroatom. This is preferable in view of the dispersibility of the inorganic compound and the reinforcing effect.

[0025] The heteroatom are atoms belonging to 2nd to 4th Periods and Group 5B or 6B in the Periodic Table, which concretely include nitrogen atom, oxygen atom, sulfur atom, phosphorus atom, silicon atom and so on. Among them, nitrogen atom, oxygen atom and so on are favorable. As the polar group containing such a heteroatom, mention may be made of a hydroxyl group, an alkoxysilyl group, an epoxy group, a carboxyl group, a carbonyl group, an oxycarbonyl group, a sulfide group, a disulfide group, a sulfonyl group, a sulfinyl group, a thiocarbonyl group, an imino group, an amino group, a nitrile group, an ammonium group, an imido group, an amido group, a hydrazo group, an azo group, a diazo group, an oxygen-containing heterocyclic group, a nitrogen-containing heterocyclic group, a sulfur-containing heterocyclic group and so on. Among them, the hydroxyl group, carboxyl group, epoxy group, sulfide group, sulfonyl group, amino group, nitrogen-containing heterocyclic group and alkoxysilyl group are favorable, and the hydroxyl group, amino group, carboxyl group, nitrogen-containing heterocyclic group and alkoxysilyl group are more favorable, and the hydroxyl group or amino group is most favorable.

[0026] The vinyl monomer having the above polar group is not particularly limited and may be a polymerizable monomer having at least one polar group in its molecule. There are concretely mentioned a hydroxyl group-containing vinyl monomer, an amino group-containing vinyl monomer, a nitrile group-containing vinyl monomer, a carboxyl group-containing vinyl monomer, an alkoxysilyl group-containing vinyl monomer and so on. Among them, the carboxyl group-containing vinyl monomer, alkoxysilyl group-containing vinyl monomer and amino group-containing vinyl monomer and so on are favorable. These polar group-containing vinyl monomers may be used alone or in a combination of two or more.

[0027] As the hydroxyl group-containing vinyl monomer among these polar group-containing vinyl monomers, mention may be made of polymerizable monomers having at least one primary, secondary or tertiary hydroxyl group in their molecules. As the hydroxyl group-containing vinyl monomer, there are mentioned, for example, a hydroxyl group-containing unsaturated carboxylic acid monomer, a vinyl ether monomer, vinyl ketone monomer and the like, among which the hydroxyl group-containing unsaturated carboxylic acid monomer is favorable. As the hydroxyl group-containing unsaturated carboxylic acid monomer, mention may be made of derivatives, esters, amides, anhydrides and the like of acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid and so on, among which ester compounds of acrylic acid, methacrylic acid and so on are favorable.

[0028] As a concrete example of the hydroxyl group-containing polymerizable monomer, mention may be made of hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate and so on; mono(meth)acrylates of polyalkylene glycols (number of alkylene glycol units is, for example, 2-23) such as polyethylene glycol, polypropylene glycol and so on; hydroxyl group-containing unsaturated amides such as N-hydroxyme-

thyl (meth)acrylamide, N,N-bis(2-hydroxyethyl) (meth)acrylamide and so on; hydroxyl group-containing vinyl aromatic compounds such as o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, o-hydroxy-α-methylstyrene, m-hydroxy-α-methylstyrene, p-hydroxy-α-methylstyrene, p-vinylbenzyl alcohol and so on; (meth)allyl alcohol and the like. Among them, the hydroxyalkyl (meth)acrylates and the hydroxyl group-containing vinyl aromatic compounds are favorable. These hydroxyl group-containing polymerizable monomers may be used alone or in a combination of two or more.

[0029] As the nitrile group-containing polymerizable monomer, mention may be made of (meth)acrylonitrile, vinylidene cyanide and so on. These nitrile group-containing vinyl monomers may be used alone or in a combination of two or more.

[0030] As the amino group-containing vinyl monomer, mention may be made of polymerizable monomers having at least one amino group selected from primary, secondary and tertiary amino groups in their molecules. Among them, tertiary amino group-containing vinyl monomers (dialkylaminoalkyl (meth)acrylates, tertiary amino group-containing vinylaromatic compounds and so on) are particularly favorable. These amino group-containing vinyl monomers may be used alone or in a combination of tow or more.

[0031] As the primary amino group-containing vinyl monomer, mention may be made of acrylamide, methacrylamide, p-aminostyrene, aminomethyl (meth)acrylate, aminoethyl (meth)acrylate, aminopropyl (meth)acrylate, aminobutyl (meth)acrylate and so on.

[0032] As the secondary amino group-containing vinyl monomer, mention may be made of (1) anilinostyrenes such as anilinostyrene, β-phenyl-p-anilinostyrene, β-cyano-p-anilinostyrene, β-cyano-β-methyl-p-anilinostyrene, β-chloro-p-anilinostyrene, β-methyl-β-methoxycarbonyl-p-anilinostyrene, β-carboxy-p-anilinostyrene, β-methoxycarbonyl-p-anilinostyrene, β-(2-hydroxyethoxy) carbonyl-p-anilinostyrene, β-formyl-p-anilinostyrene, β-formyl-β-methyl-p-anilinostyrene, α-carboxy-β-carboxy-β-phenyl-p-anilinostyrene and so on; (2) anilinophenyl butadienes such as anilinophenyl butadiene and its derivatives, for example, 1-anilinophenyl-1,3-butadiene, 1-anilinophenyl-3-methyl-1,3-butadiene, 1-anilinophenyl-3-chloro-1,3-butadiene, 3-anilinophenyl-2-methyl-1,3-butadiene, 1-anilinophenyl-2-chloro-1,3-butadiene, 2-anilinophenyl-1,3-butadiene, 2-anilinophenyl-3-methyl-1,3-butadiene, 2-anilinophenyl-3-chloro-1,3-butadiene and so on; (3) N-monosubstituted (meth)acrylamides such as N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-methylol acrylamide, N-(4-anilinophenyl) methacrylamide and so on.

[0033] As the tertiary amino group-containing vinyl monomer, mention may be made of N,N-disubstituted aminoalkyl acrylates, N,N-disubstituted aminoalkyl acrylamides, N,N-disubstituted aminoaromatic vinyl compounds, pyridine group-containing vinyl compounds and so on.

[0034] As the N,N-disubstituted aminoacrylate, mention may be made of N,N-dimethylaminomethyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-dimethylaminobutyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-diethylaminobutyl (meth)acrylate, N-methyl-N-ethylaminoethyl (meth)acrylate, N,N-dipropylaminoethyl (meth)acrylate, N,N-dibutylaminoethyl (meth)acrylate, N,N-dibutylaminopropyl (meth)acrylate, N,N-dibutylaminobutyl (meth)acrylate, N,N-dihexylaminoethyl (meth)acrylate, N,N-dioctylaminoethyl (meth)acrylate; and esters of acrylic acid or methacrylic acid such as acryloylmorpholine and so on. Among them, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-diproprylaminoethyl (meth)acrylate, N,N-dioctylaminoethyl (meth)acrylate, N-methyl-N-ethylaminoethyl (meth) acrylate and so on are favorable.

[0035] As the N,N-disubstituted aminoalkyl acrylamide, mention may be made of acrylamide compounds and methacrylamide compounds such as N,N-dimethylaminomethyl (meth)acrylamide, N,N-dimethylaminoethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, N,N-dimethylaminobutyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, N,N-diethylaminobutyl (meth)acrylamide, N-methyl-N-ethylaminoethyl (meth)acrylamide, N,N-dipropylaminoethyl (meth)acrylamide, N,N-dibutylaminoethyl (meth)acrylamide, N,N-dibutylaminopropyl (meth)acrylamide, N,N-dibutylaminobutyl (meth)acrylamide, N,N-dihexylaminoethyl (meth)acrylamide, N,N-dihexylaminopropyl (meth)acrylamide, N,N-dioctylaminopropyl (meth)acrylamide and so on. Among them, N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, N,N-dioctylaminopropyl (meth)acrylamide and so on are favorable.

[0036] As the N,N-disubstituted aminoaromatic vinyl compound, mention may be made of styrene derivatives such as N,N-dimethylaminoethyl styrene, N,N-diethylaminoethyl styrene, N,N-dipropylaminoethyl styrene, N,N-dioctylaminoethyl styrene and so on.

[0037] And also, a nitrogen-containing heterocyclic group may be used instead of the amino group. As a nitrogen-containing heterocycle, mention may be made of pyrrole, histidine, imidazole, triazolidine, triazole, triazine, pyridine, pyrimidine, pyrazine, indole, quinoline, purine, phenadine, pteridine, melamine and so on. The nitrogen-containing heterocycle may contain the other heteroatom in its ring. As the pyridyl group-containing vinyl compound, mention may be made of 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine and so on. Among them, 2-vinylpyridine and 4-vinylpyridine are favorable.

[0038] As the epoxy group-containing polymerizable monomer, mention may be made of (meth)allylglycidyl ether, glycidyl (meth)acrylate, 3,4-oxycyclohexyl (meth)acrylate and so on. These epoxy group-containing monomers may

be used alone or in a combination of two or more.

[0039] As the carboxyl group-containing polymerizable monomer, mention may be made of unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid, tetraconic acid, cinnamic acid and so on; non-polymerizable polyvalent carboxylic acids such as phthalic acid, succinic acid, adipic acid and so on; free carboxyl group-containing esters and salts thereof such as monoesters with a hydroxyl group-containing unsaturated compound such as (meth)acryl alcohol, 2-hydroxyethyl (meth)acrylate and the like. Among them, the unsaturated carboxylic acids are favorable. These carboxyl group-containing monomers may be used alone or in a combination of two or more.

[0040] As the alkoxysilyl group-containing polymerizable monomer, mention may be made of (meth)acryloxymethyl methoxysilane, (meth)acryloxymethylmethyl dimethoxysilane, (meth)acryloxymethyldimethyl methoxysilane, (meth) acryloxymethyl triethoxysilane, (meth)acryloxymethylmethyl diethoxysilane, (meth)acryloxymethyldimethyl ethoxysilane, (meth)acryloxymethyl tripropoxysilane, (meth)acryloxymethylmethyl dipropoxysilane, (meth)acryloxymethyldimethyl propoxysilane, γ-(meth)acryloxypropyl trimethoxysilane, γ-(meth)acryloxypropylmethyl dimethoxysilane, γ-(meth)acryloxypropyldimethyl methoxysilane, γ-(meth)acryloxypropyl triethoxysilane, γ-(meth)acryloxypropylmethyl diethoxysilane, γ-(meth)acryloxypropyldimethyl ethoxysilane, γ-(meth)acryloxypropyl tripropoxysilane, γ-(meth)acryloxypropylmethyl dipropoxysilane, γ-(meth)acryloxypropyldimethyl propoxysilane, γ-(meth)acryloxypropylmethyl diphenoxysilane, y-(meth)acryloxypropyldimethyl phenoxysilane, γ-(meth)acryloxypropylmethyl dibenzyloxysilane, γ-(meth)acryloxypropyldimethyl benzyloxysilane and so on. And also, the alkoxysilyl group-containing vinyl monomer includes, for example, trimethoxyvinyl silane, triethoxyvinyl silane, 6-trimethoxysilyl-1,2-hexene, p-trimethoxysilyl styrene and so on as disclosed in JP-A-7-188356. These alkoxysilyl group-containing monomers may be used alone or in a combination of two or more.

[0041] A bonding amount of the monomer in the diene-based rubber is properly selected in accordance with the required characteristics. The bonding amount of the conjugated diene monomer is usually 40-100 mass%, preferably 50-90 mass%, more preferably 60-85 mass%, and the bonding amount of the aromatic vinyl monomer is usually 0-60 mass%, preferably 10-50 mass%, more preferably 15-40 mass%. And also, when the diene-based rubber is made of a monomer containing a heteroatom-containing polar group, the bonding amount of the polar group-containing monomer is properly selected in accordance with the magnification of the polarity, but is favorable to be usually 0.01-20 mass%. When the bonding amount of the polar group-containing monomer is less than 0.01 mass%, even if the monomer has a large polarity, the interaction with the inorganic compound is small and it is difficult to obtain the sufficient effect. While, when it exceeds 20 mass%, the strong aggregation with the inorganic compound is caused to make the processing difficult. When using a copolymer rubber latex containing each of the monomers in the bonding amount of the aforementioned range, there is obtained a rubber composition having highly balanced properties of wear resistance and further lower heat build-up property and wet skid resistance.

[0042] The polymerization method for the diene-based rubber is not particularly limited and includes a radical polymerization method, an anionic polymerization method, a coordination anionic polymerization method, a cationic polymerization method and the like. As the radical polymerization method, there are a mass polymerization method, a suspension polymerization method, an emulsion polymerization method and the like. In the invention is particularly preferable the emulsion polymerization method wherein a stable emulsified dispersion is provided at the completion of the polymerization because a diene-based rubber latex is used. In this emulsion polymerization can be used a usual polymerization method, which includes a method wherein a given monomer(s) is emulsified in an aqueous medium under the presence of an emulsifyer and then polymerization is started through a radical polymerization initiator and stopped through a short-stop after a given conversion is obtained, and so on.

[0043] As the emulsifyer, mention may be made of an anionic surfactant, a nonionic surfactant, a cationic surfactant, an amphoteric surfactant and so on. And also, a fluorine-based surfactant may be used. These emulsifyers may be used alone or in a combination of two or more. Usually, the anionic surfactant, for example, a long-chain aliphatic acid salt having a carbon number of not less than 10, a rosinate or the like is frequently used. Concretely, mention may be made of potassium salts, sodium salts and the like of capric acid, lauric acid, myristic acid, palmitic acid, oleic acid and stearic acid.

[0044] As the radical polymerization initiator, use may be made of organic peroxides such as benzoyl peroxide, lauroyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, paramenthane hydroperoxide, di-tert-butyl peroxide, dicumyl peroxide and the like. And also, there may be used diazo compounds exemplified by azobisisobutyronitrile, inorganic peroxides exemplified by potassium persulfate, redox catalysts exemplified by a combination of the peroxide and ferrous sulfate, and so on. These radical polymerization initiators may be used alone or in a combination of two or more.

[0045] And also, a chain transfer agent may be used for adjusting a molecular weight of the diene-based rubber. As the chain transfer agent, use may be made of alkyl mercaptans such as tert-dodecyl mercaptan, n-dodecyl mercaptan and the like; carbon tetrachloride, thioglycols, diterpene, terpinolene, γ-terpinene and so on.

[0046] In the polymerization for the diene-based rubber, each of the monomers, the emulsifyer, the radical polymerization initiator and the chain transfer agent may be charged into a reaction vessel at once to start polymerization, or

may be continuously or intermittently added in the continuation of the reaction. Such a polymerization can be carried out at 0-100°C by using, for example, an oxygen-removed reaction vessel, and particularly it is favorable to conduct the polymerization at a polymerizing temperature of 0-80°C. On the way of the polymerization reaction, operating conditions such as temperature, stirring and the like may be changed properly. The polymerization system may be continuous or batch. Furthermore, there may be adopted a method wherein a part of the monomer, radical polymerization initiator, chain transfer agent or the like is added at a specified conversion.

[0047] Moreover, as the conversion becomes large, a tendency of gelation is recognized, so that it is favorable to control the conversion with 80%, and particularly it is preferable to stop the polymerization when the conversion is within a range of 30-70%. The stop of the polymerization is carried out by adding a short-stop when a given conversion is obtained. As the short-stop are used an amine compound such as hydroxylamine, diethyl hydroxylamine or the like; a quinone compound such as hydroquinone or the like; and so on. After the stop of the polymerization, a diene-based rubber latex to be used in the invention can be obtained by removing unreacted monomers through a method such as steam distillation or the like, if necessary.

[0048] The diene-based rubber latex can be used by dispersing an extender oil for rubber. The extender oil for rubber is not particularly limited, so that a process oil such as naphtenic, paraffinic or aromatic oil can be used. An amount of the extender oil for rubber dispersed in the diene-based rubber latex is preferable to be 5-100 parts by mass, particularly 10-60 parts by mass based on 100 parts by mass of a diene-based rubber included in the diene-based rubber latex.

[0049] The diene-based rubber used in the invention is favorable to have a Moony viscosity [ML_{1+4}(100°C)] of 10-200, particularly 30-150. When the Moony viscosity is less than 10, the properties inclusive of wear resistance are insufficient, while when it exceeds 200, the processability is poor and the milling is difficult. The Moony viscosity may be a value of a rubber without the extender oil or a rubber with the extender oil.

[0050] As the inorganic compound to be mixed with the diene-based rubber is used silica or a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10). Moreover, the compound of the formula (I) is an inorganic compound but does not include a metal itself.

[0051] As a concrete example of the compound of the formula (I), mention may be made of alumina (Al_2O_3) such as γ-alumina, α-alumina or the like; an alumina monohydrate ($Al_2O_3 \cdot H_2O$) such as boehmite, diaspore or the like; aluminum hydroxide ($Al(OH)_3$) such as gibbsite, bayerite or the like; magnesium oxide (MgO), magnesium hydroxide ($Mg(OH)_2$), calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), aluminum magnesium oxide ($MgO \cdot Al_2O_3$), titanium white (TiO_2) such as rutile, anatase or the like; titanium black (TiO_{2n-1}), calcined clay ($Al_2O_3 \cdot 2SiO_2$), kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$), bentonite ($Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$), talc ($3MgO \cdot 4SiO_2 \cdot H_2O$), attapulgite ($5MgO \cdot 8SiO_2 \cdot 9H_2O$), aluminum silicate ($Al_2SiO_5$, $Al_4 \cdot 3SiO_4 \cdot 5H_2O$, or the like), magnesium calcium silicate ($CaMgSiO_4$), aluminum silicate (Al_2SiO_5, $Al_4 \cdot 3SiO_2 \cdot 5H_2O$ or the like), magnesium silicate ($MgSiO_3$), calcium silicate ($CaO \cdot SiO_2 \cdot yH_2O$), and a crystalline aluminosilicate containing a hydrogen or an alkali metal or an alkaline metal for correcting an electric charge such as various zeolites, and so on.

[0052] Among the compounds of the formula (I), a compound represented by the following formula (II):

$$Al_2O_3 \cdot mSiO_2 \cdot nH_2O \qquad (II)$$

(wherein m is a number of 0-4 and n is a number of 0-4) is particularly favorable. As a concrete example of such a compound, mention may be made of alumina such as γ-alumina, α-alumina or the like; aluminum monohydrate such as boehmite, diaspore or the like; aluminum hydroxide such as gibbsite, bayerite or the like; calcined clay, kaolin, pyrophyllite, bentonite and so on.

[0053] And also, silica is not particularly limited, and silica generally used as a filler in a rubber composition can be used. Concretely, silica having a nitrogen adsorption specific surface area (BET value) of 50-650 g/m^2, preferably 100-400 g/m^2 is favorable.

[0054] The inorganic compound used in the invention is favorable to have a particle size of not more than 10 μm, preferably not more than 3 μm. As the particle size of the inorganic compound becomes large, it unfavorably tends to degrade fatigue resistance and wear resistance of rubber.

[0055] Moreover, powdery inorganic compounds used in the invention may be used alone or in an admixture of two or more.

[0056] An amount of the inorganic compound introduced into the diene-based rubber-inorganic compound composite material obtained by the method of the invention is favorable to be within a range of 5-200 parts by mass per 100 parts by mass of the diene-based rubber in the composite material. When the introduction amount is less than 5 parts by mass, the improvement of gripping performance on wet road surface is hardly obtained, while when the introduction amount exceeds 200 parts by mass, there are unfavorably caused problems that the dispersibility of the inorganic compound into the diene-based rubber is degraded and the composite material becomes considerably hard and the production of the composite material is difficult and the like.

[0057] The "dispersion of inorganic compound" in the invention may be one obtained by dispersing the aforementioned inorganic compound into an aqueous medium such as water or the like through stirring. For instance, the inorganic compound, for example, commercially available powder of silica (SiO_2), alumina (Al_2O_3) such as γ-alumina, α-alumina or the like; an alumina monohydrate (Al_2O_3-H_2O) such as boehmite, diaspore or the like; aluminum hydroxide ($Al(OH)_3$) such as gibbsite, bayerite or the like; magnesium oxide (MgO), magnesium hydroxide ($Mg(OH)_2$), calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), aluminum magnesium oxide ($MgO \cdot Al_2O_3$), titanium white (TiO_2) such as rutile, anatase or the like; titanium black (TiO_{2n-1}), calcined clay, kaolin, pyrophyllite, bentonite, talc, attapulgite, aluminum silicate (Al_2SiO_5, $Al_4 \cdot 3SiO_4 \cdot 5H_2O$, or the like), magnesium calcium silicate, magnesium silicate, calcium silicate-aluminosilicate or the like can be finely dispersed into the aqueous medium such as water or the like through shear stirring. In this case, there can be used, for example, a colloid mill, an oscillation mill, a homogenizer, a dyno mill, a tube mill, a super-mill or the like.

[0058] And also, the "dispersion of inorganic compound" may be prepared by adding an acid or an alkali to an aqueous solution of an inorganic salt capable forming the inorganic compound of the formula (I). As a concrete preparation method for the dispersion of the inorganic compound, (1) a compound obtained by gelating a basic aluminum salt through heating and neutralizing with a base, or (2) an alumina gel obtained by adding and neutralizing with an aluminum salt such as aluminum chloride and an aluminate, or (3) a precipitate of aluminum hydroxide formed by reacting an aluminate with a mineral acid or the like or reacting an aluminum salt such as aluminum sulfate with an alkali such as caustic soda or the like can be finely dispersed into an aqueous medium such as water or the like through shear stirring likewise the above case.

[0059] The inorganic salt is not particularly limited unless it can form the inorganic compound of the formula (I), and may be at least one inorganic salt selected from the group consisting of metal salts and oxo acid salts of metals. For instance, there are mentioned (1) aluminum salts such as aluminum chloride, aluminum nitrate, aluminum sulfate, basic aluminum chloride, basic aluminum sulfate, aluminum polychloride and the like; (2) calcium nitrite, calcium sulfate, calcium chloride, magnesium chloride (hexahydrate), magnesium nitrate (hexahydrate), magnesium sulfate, titanium trichloride, titanium tetrachloride and the like; (3) an aluminate (oxo acid salt of aluminum) such as sodium aluminate, and so on. Then, an aqueous solution of the inorganic salt is prepared and, if necessary, a pH of the aqueous solution is adjusted with a mineral acid or an alkali, and mixed with the diene-based rubber latex. Such compounds may be used alone or in an admixture of two or more.

[0060] And also, an alumina sol prepared by deflocculating an alumina gel made from sodium aluminate, aluminum sulfate or the like through a method as disclosed in JP-B-40-8409 or the like can be used as an aqueous dispersion.

[0061] Furthermore, the "dispersion of inorganic compound" can be prepared by adding water, an acid or an alkali to a solution of an organic metal compound capable of forming the inorganic compound of the formula (I). As the organic metal compound, mention may be made of various metal alkoxides such as triethoxy aluminum, tripropoxy aluminum, diethoxy magnesium, dipropoxy magnesium, tetraethoxy titanium and tetrapropoxy titanium, or organic metal compounds wherein at least one of the alkoxides is substituted with a hydrolyzable halogen such as chlorine or the like, and alkylsilicates and so on. And also, the solution of the organic metal compound is mainly a solution dissolved in an organic solvent. As the organic solvent, it is favorable to use a water-soluble methanol, ethanol, isopropanol, ethylene glycol, dimethyl acetoamide, methyl ethyl ketone or the like. The inorganic compound can be formed by reacting the solution of the organic metal compound with water to hydrolyze the organic metal compound or by condensing the resulting hydrolyzate. In the reaction between the organic metal compound and water, an acid or an alkali may be added alone or as an aqueous solution, if necessary, in order to promote condensation reaction. And also, the solution of the organic metal compound may be mixed with an aqueous solution of the above inorganic salt to prepare a dispersion of an inorganic compound.

[0062] In addition, the "dispersion of inorganic compound" can be prepared by adding and reacting an alkali (for example, aqueous solution of sodium hydroxide or the like) to a metal shown in the formula (I) (for example, Al or the like). In this case, one metal may be used, or two or more metals may be used.

[0063] Next, the above aqueous dispersion of the inorganic compound is mixed with an aqueous dispersion of the diene-based rubber. The term "aqueous dispersion" used herein means that the rubber component or the inorganic compound is not necessarily required to be completely dissolved in water and includes a mixed solution after the emulsion polymerization, or a colloidal solution of the inorganic compound.

[0064] Especially, the aqueous dispersion of the inorganic compound is favorable to have pH of 8.5-11 or 2-4. In this

case, it is desirable to readjust pH before the formation of the rubber composition by mixing with the other compounding chemicals and the like.

[0065] And also, silicon salt (silicon chloride or the like) and/or oxo acid salt of silicon (silicate of sodium silicate) can be added to the aqueous dispersion. In this case, the silicate and aluminum salt or aluminate may be mixed as the same aqueous solution with the latex or may be prepared into separate aqueous solutions and mixed with the latex.

[0066] In any case, the diene-based rubber-inorganic compound composite material according to the invention can be produced by mixing the dispersion of the diene-based rubber with the dispersion of the inorganic compound, or through a step of mixing the aqueous dispersion of the diene-based rubber with the aqueous solution of the inorganic salt capable of forming the inorganic compound of the formula (I) or the solution of the organic metal compound capable of forming the inorganic compound of the formula (I) as mentioned above.

[0067] Then, the diene-based rubber-inorganic compound composite material is usually taken out from a mixture of the aqueous dispersion of the diene-based rubber and the aqueous dispersion of the inorganic compound or the aqueous solution of the inorganic compound. As a method of taking out the diene-based rubber-inorganic compound composite material from a mixed solution of the aqueous dispersion of the diene-based rubber and the aqueous dispersion of the inorganic compound or the aqueous solution of the inorganic compound, there can be used a method wherein it is taken out as a coagulated mass likewise a general coagulation method, or a method wherein the aqueous medium is removed by a method such as heating, pressure reducing or the like. The former method is preferable in a point that a more uniform diene-based rubber-inorganic compound composite material can be obtained. In each of these methods, pH of the mixed solution may be previously adjusted, if necessary. And also, an emulsified mass of an extender oil for rubber usually used may be mixed to take out an oil-extended rubber-inorganic compound composite material.

[0068] As the coagulation method, for example, the diene-based rubber-inorganic compound composite material can be coagulated as a crumb by adding (1) sodium chloride, potassium chloride which are components constituting an electrolyte, (2) a salt of a polyvalent metal such as calcium, magnesium, zinc, aluminum or the like, e.g. calcium chloride, magnesium chloride, zinc chloride, aluminum chloride, calcium nitrate, magnesium nitrate, zinc nitrate, aluminum nitrate, magnesium sulfate, zinc sulfate, aluminum sulfate or the like, and/or, if necessary, (3) hydrochloric acid, nitric acid, sulfuric acid or the like. Among them, the salt of the polyvalent metal such as calcium, magnesium, aluminum or the like is favorable, and calcium chloride, magnesium chloride and magnesium sulfate are particularly preferable. They may be used alone or in a combination of two or more.

[0069] In this case, fine inorganic compound may be flocculated by using a polymer flocculating agent (particularly anionic and nonionic among anionic, nonionic and cationic). Particularly, temperature, pH and the like are not limited when the diene-based rubber-inorganic compound composite material is coagulated as a crumb or co-coagulated, but it is favorable that in order to reduce inorganic salt remaining in the resulting diene-based rubber-inorganic compound composite material, the temperature is controlled above 10°C and the pH value is controlled to a range of 2-14 (particularly acidic side, e.g. pH = 3-6).

[0070] A method of drying a coagulated mass after the diene-based rubber and the inorganic compound are co-coagulated is not particularly limited. For example, there is a method wherein the coagulated mass is washed with water to remove the emulsifyer, the electrolyte and the like and then subjected to a hot drying, a drying under vacuum or the like to remove water. In this way can be produced a composite material wherein the inorganic compound is uniformly dispersed in the diene-based rubber. As the method of removing the aqueous medium from the mixture, there are mentioned a method wherein the mixed solution is subjected to a cast drying and dried under vacuum, a drying method through a drum dryer and so on.

[0071] When the diene-based rubber-inorganic compound composite material produced by the method of the invention is put into a practical use, it is usually compounded with a crosslinking agent including of a vulcanizing agent and the like to form a rubber composition, and may be further compounded with the other rubber component, a reinforcing filler, the other filler, a coupling agent, a vulcanization accelerator, an aliphatic acid and the like.

[0072] The crosslinking agent to be compounded in the rubber composition according to the invention includes a vulcanizing agent such as sulfur, other sulfur-containing compound or the like, or a crosslinking agent containing no sulfur such as a peroxide or the like, but the vulcanizing agent, particularly sulfur is favorable. The crosslinking agent is favorable to be compounded in an amount of 0.5-10 parts by mass, preferably 1-6 parts by mass based on 100 parts by mass of the rubber component.

[0073] The other rubber component to be compounded in the rubber composition according to the invention is not particularly limited, but includes styrene-butadiene copolymer rubber, butadiene rubber, isoprene rubber, butadiene-isoprene copolymer rubber, butadiene-styrene-isoprene copolymer rubber, acrylonitrile-butadiene copolymer rubber, acrylonitrile-styrene-butadiene copolymer rubber, acrylic rubber, butyl rubber, natural rubber, chloroprene rubber and so on. Further, the diene-based rubber having a heteroatom-containing functional group used in the invention can be additionally used as the other rubber component.

[0074] As the reinforcing filler, mention may be made of carbon black, silica and inorganic fillers represented by the above formula (I). As the carbon black, there are channel black, furnace black, acetylene black, thermal black and so

on in accordance with production methods, all of which blacks can be used. The carbon black is favorable to have a nitrogen adsorption specific surface area (BET value) of not less than 70 m^2/g and a dibutyl phthalate absorption (DBP) of not less than 90 ml/100 g.

[0075] When the BET value is less than 70 m^2/g, it is difficult to obtain a sufficient wear resistance, and as the BET value becomes too large, low fuel consumption property tends to be degraded. Considering the wear resistance and low fuel consumption property, a more preferable range of the BET value is 90-180 m^2/g. Moreover, the BET value is a value measured according to ASTM D3037-88. On the other hand, when the DBP value is less than 90 ml/100 g, the sufficient wear resistance is hardly obtained, and as the DBP value becomes too large, the elongation at break of the rubber composition is degraded. Considering the wear resistance and low fuel consumption property, a more preferable range of the DBP value is 100-180 ml/100 g. Moreover, the DBP value is a value measured according to JIS K6221-1982 (method A).

[0076] The silica is not particularly limited and can be used by properly selecting from those usually used for the reinforcement of rubber such as dry-process silica, wet-process silica (precipitated silica) and so on, but the wet-process silica is favorable. The silica is preferable to have a nitrogen adsorption specific surface area (BET value) of 100-300 m^2/g considering the wear resistance and low fuel consumption property. Moreover, the BET value is a value measured according to ASTM D4820-93 after being dried at 300°C for 1 hour.

[0077] In the invention, only the carbon black may be used, or only the silica may be used, or the carbon black and the silica may be used together. And also, an amount of the reinforcing filler compounded is preferable to be a range of 5-85 parts by mass based on 100 parts by mass of the rubber component from a viewpoint of the balance among the wear resistance, wet performances and low fuel consumption and so on.

[0078] As the other filler, mention may be made of calcium carbonate, magnesium carbonate and so on.

[0079] A coupling agent is not particularly limited, but a silane coupling agent is favorable. As the silane coupling agent, mention may be made of vinyl trichlorosilane, vinyl triethoxysilane, vinyl tris(β-methoxy-ethoxy) silane, β-(3,4-epoxycyclohexyl)-ethyl trimethoxysilane, γ-glycidoxypropyl trimethoxysilane, γ-glycidoxypropylmethyl diethoxysilane, γ-methacryloxypropyl trimethoxysilane, N-(β-aminoethyl)-γ-aminopropyl trimethoxysilane, N-(β-aminoethyl)-γ-aminopropyl trimethyl dimethoxysilane, N-phenyl-γ-aminopropyl trimethoxysilane, γ-chloropropyl trimethoxysilane, γ-mercaptopropyl trimethoxysilane, γ-aminopropyl trimethoxysilane, bis(3-(triethoxysilyl)propyl) tetrasulfide, bis(3-(triethoxysilyl)propyl) disulfide, γ-trimethoxysilyl propyl dimethyl thiocarbamyl tetrasulfide, γ-trimethoxysilyl propyl benzothiazyl tetrasulfide and so on. As the coupling agent is compounded, the wear resistance or tan δ is more improved. The amount of the coupling agent compounded is favorable to be not more than 20 parts by mass, particularly not more than 15 parts by mass (usually not less than 1 part by mass) based on 100 parts by mass of the inorganic compound included in the rubber composition or 100 parts by mass in total of the inorganic compound and the inorganic filler additionally compounded such as the reinforcing filler or the like.

[0080] As the vulcanization accelerator, use may be made of an aldehyde ammonia system, a guanidine system, a thiourea system, a thiazol system, a dithiocarbamic acid system and so on. It is favorable to be compounded in an amount of 0.5-15 parts by mass, particularly 1-10 parts by mass based on 100 parts by mass of the rubber component.

[0081] The aliphatic acids include an aliphatic acid, an ester compound thereof and so on. As the aliphatic acid, a higher aliphatic acid is favorable and is usually a monocarboxylic acid having a carbon number of not less than 10 (preferably not less than 12, usually not more than 20), which may be a saturated aliphatic acid or an unsaturated aliphatic acid, but the saturated aliphatic acid is preferable in view of a weather resistance. As such an aliphatic acid, mention may be made of palmitic acid, stearic acid, oleic acid, linolic acid, linolenic acid and so on.

[0082] As the ester compound of the aliphatic acid, an ester of an alcohol compound with the above higher aliphatic acid is favorable. The carbon number of the alcohol compound is not particularly limited, but it is usually about 1-10. And also, an ester of a lower aliphatic acid (carbon number of about 1-10) with a higher alcohol (carbon number of not less than about 10 but not more than about 20) may be used.

[0083] The rubber composition according to the invention may be further compounded with an extender oil for rubber such as naphthenic, paraffinic, aromatic process oils and the like. As the extender oil, the aromatic or naphthenic process oil is favorable. Furthermore, zinc oxide, an accelerator activator, an antioxidant, a processing aid and the like may be compounded in proper amounts.

[0084] A rubber article can be manufactured by using the rubber composition according to the invention as follows. That is, the diene-based rubber-inorganic compound composite material and, if necessary, the other rubber component, and the reinforcing agent such as silica, carbon black, carbon-silica dual phase filler or the like, the extender oil for rubber, the other compounding agents are first milled at a temperature of 70-180°C by using a milling machine such as a Banbury mixer or the like. Thereafter, the milled mass is cooled and further compounded with a vulcanizing agent such as sulfur or the like, a vulcanization accelerator and so on in a Banbury mixer, a mixing rolls or the like and then shaped into a given form. Then, the thus shaped body is cured at 140-180°C to obtain a required rubber vulcanizate or a rubber article.

[0085] This rubber vulcanizate has excellent tensile strength, wear resistance, wet skid resistance, rebound resilience

and the like. And also, an uncured rubber has a good processability. Therefore, the rubber compositions according to the invention can be used as a rubber article in various fields owing to its excellent properties. For example, they can be used for a tread, a base tread, a sidewall, an abrasion and the like of tires for large-size vehicles and passenger cars; industrial goods such as a rubber roll, a rice husking roll, a belt, a hose, a sponge, a rubber sheet, a rubberized cloth and the like, footwear members such as transparent shoes, general-purpose color shoes, a sponge shoe bottom and the like; sanitary goods such as a sanitary skin, medical supplies and so on. They are particularly suitable as a tire tread for an automobile.

BEST MODE FOR CARRYING OUT THE INVENTION

[0086] The invention will be concretely described with respect to the following examples below.

1. Synthesis of diene-based rubber (extended with an oil and not extended with oil)

(1) Synthesis of oil-extended diene-based rubber

[0087] Into a polymerization vessel purged with nitrogen are charged 200 parts by mass of water, 4.5 parts by mass of rosin acid soap, given compounding amounts of butadiene and other monomers shown in Table 1 (unit is parts by mass, provided that a total amount of monomers is 100 parts by mass), and 0.3 part by mass of t-dodecylmercaptan. Thereafter, a temperature of the polymerization vessel is set to 5°C, and 0.1 part by mass of p-menthane hydroperoxide as a polymerization initiator, 0.07 part by mass of sodium ethylenediamine tetraacetate, 0.05 part by mass of ferrous sulfate heptahydrate and 0.15 part by mass of sodium formaldehyde sulphoxylate are added to start polymerization, and when a conversion reaches 60%, diethylhydroxyamine is added to stop the polymerization. Then, unreacted monomers are recovered by steam stripping to obtain each aqueous dispersion of diene-based rubbers having a solid content of about 21%.

[0088] Thereafter, each aqueous dispersion of the diene-based rubber is mixed with an emulsified mass containing 37.5 parts by mass of an aromatic oil (made by Fuji Kosan Co., Ltd. trade name "Fukkol-Aromax#3") based on 100 parts by mass of the solid content in the dispersion and coagulated with sulfuric acid and sodium chloride to form a crumb, which is washed with water and dried in a hot dryer to obtain an oil-extended diene-based rubber (A to J in Table 1). The monomer bonding content (bonding contents of styrene, monomer containing carboxylic acid group, monomer containing amino group and nitrile group, monomer containing hydroxyl group, butyl acrylate and monomer containing alkoxysilyl group) and Mooney viscosity of the oil-extended diene-based rubbers (A to J in Table 1, which are shown by "Polymer" in Tables 6-13) are measured by the following methods to obtain results as shown in Table 1.

(a) Bound styrene content (mass%); It is measured from a calibration curve prepared by an infrared absorption spectroscopy.
(b) Contents of 1,2-vinyl bond and 1,4-trans bond of butadiene unit (mass%); They are measured by an infrared absorption spectroscopy (Morello's method).
(c) Bonding content of monomer containing carboxylic acid group (mass%); It is measured by neutralization titration after the rubber is dissolved in toluene and purified by subjecting to reprecipitation with methanol two times and dried under vacuum and then the rubber is dissolved in chloroform.
(d) Bonding content of monomer containing amino group and nitrile group (mass%); It is measured from a nitrogen content through an elementary analysis after the rubber is dissolved in toluene and purified by subjecting to reprecipitation with methanol two times and dried under vacuum.
(e) Bonding content of monomer containing hydroxyl group (mass%); It is measured by ^{1}H-NMR at 270 MHz after the rubber is dissolved in toluene and purified by subjecting to reprecipitation with methanol two times and dried under vacuum.
(f) Bonding content of butyl acrylate (mass%); It is measured by ^{13}C-NMR at 270 MHz after the rubber is dissolved in toluene and purified by subjecting to reprecipitation with methanol two times and dried under vacuum.
(g) Bonding content of monomer containing alkoxysilyl group (mass%); It is measured by ^{1}H-NMR at 270 MHz after the rubber is dissolved in toluene and purified by subjecting to reprecipitation with methanol two times and dried under vacuum.
(h) Mooney viscosity [ML_{1+4}(100°C)]; It is measured at a measuring temperature of 100°C according to JIS K6300-1994 after 4 minutes through a preliminary heating for 1 minute.

(2) Synthesis of diene-based rubber (not extended with oil)

[0089] Into a polymerization vessel purged with nitrogen are charged 200 parts by mass of water, 4.5 parts by mass

of rosin acid soap, given compounding amounts of butadiene and other monomers shown in Table 2 (unit is parts by mass, provided that a total amount of monomers is 100 parts by mass), and 0.3 part by mass of t-dodecylmercaptan. Thereafter, a temperature of the polymerization vessel is set to 5°C, and 0.1 part by mass of p-menthane hydroperoxide as a polymerization initiator, 0.07 part by mass of sodium ethylenediamine tetraacetate, 0.05 part by mass of ferrous sulfate heptahydrate and 0.15 part by mass of sodium formaldehyde sulphoxylate are added to start polymerization, and when a conversion reaches 60%, diethylhydroxyamine is added to stop the polymerization. Then, unreacted monomers are recovered by steam stripping to obtain each aqueous dispersion of diene-based rubbers having a solid content of 21%.

[0090] Thereafter, each aqueous dispersion of the diene-based rubbers (K to T in Table 2) is coagulated with sulfuric acid and sodium chloride to form a crumb, which is dried in a hot dryer to obtain a diene-based rubber (K to T in Table 2, which are shown by "Polymer" in Tables 6-13). The bound styrene content and Mooney viscosity of the diene-based rubbers (K to T in Table 2) are measured by the aforementioned methods to obtain results as shown in Table 2.

2. Production of composite material

(1) Use of aqueous dispersion of oil-extended diene-based rubber (A to J in Table 1)

[0091] Each of the aqueous dispersions of oil-extended diene-based rubbers (A to J in Table 1) is mixed with an emulsified mass containing 37.5 parts by mass of an aromatic oil based on 100 parts by mass of the solid content in the dispersion (Moreover, total amount of rubber and oil is 137.5 parts by mass, see Table 3). Furthermore, the mixture is mixed with an aqueous dispersion formed by dispersing 30 parts by mass of each of inorganic compounds shown in Table 5, 6, 7, 11 and 13 (aluminum hydroxide, alumina monohydrate and so on) in 200 parts by mass of water in a homomixer. Moreover, the compounding method and compounding ratio of the rubber and the inorganic compound are shown by compounding recipe A and compounding recipe D in Table 3, wherein the kind of the inorganic compound used is shown in Tables 6 and 7 (compounding recipe A) and Table 11 (compounding recipe D) and Table 13 (compounding recipe A and D).

[0092] Then, the resulting mixture is coagulated with calcium chloride to form a crumb while adjusting pH to 4-5 with sulfuric acid, which is washed with water and dried in a hot dryer to obtain an oil-extended diene-based rubber-inorganic compound composite material (composite materials of various combinations shown in Tables 3, 6, 7 and 13).

[0093] The thus obtained composite material is ashed by heating in an electric furnace at 640°C for 8 hours. An introduction amount of the inorganic compound calculated from the resulting ash content is 30 parts by mass in either compounding recipe A and D as converted into the inorganic compound based on 100 parts by mass of the diene-based rubber (see compounding recipe A and D in Table 3).

(2) Use of aqueous dispersion of diene-based rubber not extended with oil (K to T in Table 2)

[0094] The same procedure as in the above case (1) is repeated except that 37.5 parts by mass of the aromatic oil used in the above case (1) of the aqueous dispersion of the oil-extended diene-based rubber is not used and the inorganic compound is used in an amount of 20 parts by mass or 50 parts by mass (see Table 3) to obtain non oil-extended diene-based rubber-inorganic compound composite materials (composite materials of various combinations shown in compounding recipe B and C in Table 3, Tables 8, 9 (compounding recipe B), Table 10 (compounding recipe C) and Table 13 (compounding recipe B and C)).

[0095] Furthermore, composite materials shown in Table 3 (compounding recipe E) and Tables 12 and 13 (compounding recipe E) are produced by the same manner as mentioned above in case of diene-based rubbers (not extended with oil) made of E-BR and NR. In these composite materials, the introduction amount of the inorganic compound calculated from the ash content is shown in Table 3.

(3) Case through in-Situ ①

[0096] The aqueous dispersion of the diene-based rubber (A to T in Tables 1 and 2) is mixed with an emulsified mass containing 37.5 parts by mass of an aromatic oil based on 100 parts by mass of the solid content in the dispersion or a dispersion omitting the oil. Further, it is mixed with a given amount of an aqueous solution of 20 mass% sodium aluminate (compounding recipe A and D: 110 parts by mass, compounding recipe B: 75 parts by mass, compounding recipe C: 185 parts by mass, compounding recipe E: 105 parts by mass) (see Tables 6, 8, 10-13).

[0097] Then, the resulting mixture is coagulated with aluminum sulfate to form a crumb while adjusting pH to 4-5 with sulfuric acid, which is washed with water and dried in a hot dryer to obtain an oil-extended or non oil-extended diene-based rubber-inorganic compound composite material (see compounding recipe A to D in Table 3, and Tables 6, 8, 10-13). The introduction amount of the inorganic compound calculated from the ash content of the resulting

composite material is shown in Table 3 as converted by aluminum hydroxide (trade name, Higilite H-43M, made by Showa Denko Co., Ltd.).

(4) Case through in-Situ ②

[0098] The aqueous dispersion of the diene-based rubber (A to T in Tables 1 and 2) is mixed with an emulsified mass containing 37.5 parts by mass of an aromatic oil based on 100 parts by mass of the solid content in the dispersion or a dispersion omitting the oil. Further, it is mixed with an aqueous solution formed by adding 180 parts by mass of sodium hydroxide to a given amount of an aqueous solution of 20 mass% sodium aluminate (compounding recipe A and D: 110 parts by mass, compounding recipe B: 75 parts by mass, compounding recipe C: 185 parts by mass, compounding recipe E: 105 parts by mass) and adjusting pH to 14 (see Tables 6, 8, 10-13).

[0099] Then, the resulting mixture is coagulated with aluminum sulfate to form a crumb while adjusting pH to 4-5 with sulfuric acid, which is washed with water and dried in a hot dryer to obtain an oil-extended or non oil-extended diene-based rubber-inorganic compound composite material (see compounding recipe A to D in Table 3, and Tables 6, 8, 10-13). The introduction amount of the inorganic compound calculated from the ash content of the resulting composite material is shown in Table 3 as converted by aluminum hydroxide (Higilite H-43M).

3. Rubber composition and evaluation of its properties

[0100] A comparison test is conducted between a case using the above produced composite material (Examples 1-175, see Tables 6-13) and a case of dry-milling starting components by the conventional method (Comparative Examples 1-115, see Tables 6-13). In each comparative example of the latter case, starting components shown in Table 4 (not composite material) are compounded and milled at two-stage step of first stage and second stage and cured to obtain a given rubber composition and a rubber article. Moreover, the followings are used as a starting component shown in the same table. N339: trade name "Seast KH", carbon black, made by Tokai Carbon Co., Ltd. Silica: trade name "Nipsil AQ", made by Nippon Silica Industrial Co., Ltd. Aromatic oil: trade name "Fukkol-Aromax#3", made by Fuji Kosan Co., Ltd. 6C: trade name "Nocrac 6C", made by Ohuchi Shinko Chemical Industrial Co., Ltd.

Si69: trade name "Si69", made by Degusa AG

DPG: diphenylguanidien, trade name "Nocceler D", made by Ohuchi Shinko Chemical Industrial Co., Ltd.

DM: dibenzothiazyl disulfide, trade name "Nocceler DM", made by Ohuchi Shinko Chemical Industrial Co., Ltd.

NS: N-t-butyl-2-benzothiazoyl sulfenamide, trade name "Nocceler NS-F', made by Ohuchi Shinko Chemical Industrial Co., Ltd.

[0101] In each example of the former case, the same milling as in the above case is conducted by using each composite material shown in Table 3 (for example, a composite material made of 137.5 parts by mass of oil-extended diene-based rubber and 30 parts by mass of inorganic compound in compounding recipe A of Table 3 or the like) instead of diene-based rubber and inorganic compound shown in Table 4 (comparative example) (for example, a mixture of 137.5 parts by mass of oil-extended diene-based rubber and 30 parts by mass of inorganic filler in compounding recipe A of table 4). The milling method of first stage and second stage is as follows.

(Milling method of first stage)

[0102] The above obtained diene-based rubber and diene-based rubber-inorganic compound composite material are used and milled with rubber ingredients (compounding agents) in a first column of Table 4 according to a compounding recipe of Table 4 in a laboratory plastomill (made by Toyo Seiki Seisakusho) at a maximum temperature of 160°C.

(Milling method of second stage)

[0103] The thus obtained rubber composition is used and milled with rubber ingredients in a second column of Table 4. In this case, however, the milling is carried out in the same method as mentioned above except that a maximum temperature is 100°C.

[0104] The rubber composition obtained in the above method is cured at 160°C for 15 minutes to obtain a vulcanizate, and the following properties of the vulcanizate are evaluated to obtain results as shown in Tables 6-12 and Table 13 summarizing them.

① Tensile properties: A test piece of pattern No. 3 is used and a tensile strength Tb (MPa) is measured according to JIS K6251-1993 under conditions that a measuring temperature is 25°C and a tensile rate is 500 mm/min, and also a tensile stress (M_{300}) at an elongation of 300% is measured.

② Wear resistance: An abrasion loss is calculated at a slip rate of 25% by using a Lambourn abrasion tester. The measuring temperature is 25°C. A reciprocal of the abrasion loss is represented by an index on the basis that the comparative example is 100, wherein the larger the index value, the better the wear resistance.

③ Low heat build-up property: Tan δ (50°C) is measured at a temperature of 50°C and a strain of 5% and a frequency of 15 Hz by using a viscoelasticity measuring apparatus (made by Rheometrix). The smaller the tan δ (50°C), the lower the heat build-up property.

④ Rebound resilience: It is measured at a temperature of 25°C by a Dunlop tripsometer (BS903).

Table 1

		Oil-extended rubbers									
Oil-extended diene-based rubber		A	E	B	C	D	F	G	H	I	J
Feed amount (part by mass)	butadiene	58	66	57.5	57	57	57	57	51	56	57.5
	styrene	42	26	42	42	42	42	42	42	42	42
	acrylonitrile		8								
	2-hydroxyethyl methacrylate			0.5							
	diethylaminoethyl methacrylate				1						
	4-vinylpyridine					1					
	methacrylic acid						1				
	itaconic acid							1			
	butyl acrylate								7		
	methacrylamide									2	
	γ-methacryloxypropyl methacrylate										0.5
Bonding content (mass %)	styrene	35	20	35	35	35	35	35	35	35	35
	acrylonitrile		10								
	2-hydroxyethyl methacrylate			0.3							
	diethylaminoethyl methacrylate				0.7						
	4-vinylpyridine					0.6					
	methacrylic acid						0.8				
	itaconic acid							0.6			
	butyl acrylate								4		
	methacrylamide									0.9	
	γ-methacryloxypropyl methacrylate										0.4
Extender oil (part by mass)		37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5
Mooney viscosity after oil extension		50	52	48	51	52	49	48	53	51	52

Table 2

Non-oil extended rubber											
Diene-based rubber		K	N	L	M	O	P	Q	R	S	T
Feed amount (part by mass)	butadiene	72	76	71.5	71	71	100	92	99.5	99	99
	styrene	28	16	28	28	28					
	acrylonitrile		8					8			
	2-hydroxyethyl methacrylate			0.5					0.5		
	diethylaminoethyl methacrylate				1					1	
	itaconic acid					1					1
Bonding content (mass %)	styrene	23.5	13	23.5	23.5	23.5	0	0	0	0	0
	acrylonitrile		10					10			
	2-hydroxyethyl methacrylate			0.3					0.3		
	diethylaminoethyl methacrylate				0.7					0.7	
	itaconic acid					0.6					0.6
Mooney viscosity		50	48	47	51	48	48	50	50	52	49

Table 3

Components constituting composite material/ compounding recipe	A	B	C	D	E
Diene-based rubber					
oil-extended diene based rubber A-J	137.5			137.5	
non-oil extended diene based rubber K-T		100	100		
E-BR					70
NR					30
Inorganic compound	30	20	50	30	20

Table 4

Milling stages	Compounding recipe	A	B	C	D	E
First stage	oil-extended diene-based rubber	137.5			137.5	
	non-oil extended diene based rubber		100	100		
	E-BR					70
	NR					30
	N339	60	40		30	40
	silica				30	
	inorganic compound	30	20	50	30	20
	aromatic oil		10	10		10
	stearic acid	2	2	2	2	2
	6C	1	1	1	1	1
	Si69				3	1
Second stage	ZnO	3	3	3	3	3
	DPG	0.8	0.8	1.2	0.8	0.8
	DM	1	1	1.5	1	1
	NS	1	1	1	1	1
	sulfur	1.5	1.5	1.5	1.5	1.5
unit: nart by mass						

Table 5

Chemical name	Maker	Trade mark	Average particle size (μm)
Aluminum hydroxide (gibbsite)	Showa Denko Co., Ltd.	Higilite H-43M	0.6
Alumina monohydrate (boehmite)	Condea Japan Co., Ltd.	PURAL200	0.14
γ-alumina	Baikowski	Baikalox CR125	0.3
Kaolin clay	J.M.HUBER	Polyfil DL	1.0
Calcined clay	J.M.HUBER	Polyfil 40	1.2
Magnesium hydroxide	Kyowa Kagaku Kogyo Co., Ltd.	Kisma 5A	0.8
Titanium oxide (anatase)	Ishihara Sangyo Kaisha Ltd.	Tipaque A-100	0.15
Aluminum hydroxide in situ①	from sodium aluminate		
Aluminum hydroxide in situ②	from aluminum sulfate		

Table 6

Compounding recipe A

Inorganic compound	Aluminum hydroxide (gibbsite)									
Blending method	DRY									
	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10
Polymer	A	B	C	D	E	F	G	H	I	J
Tb	20.1	21.7	21.4	21.3	21.6	21.0	21.4	20.9	21.1	22.1
Wear resistance	100	110	109	108	115	107	109	108	108	113
Blending method	Aqueous dispersion									
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Polymer	A	B	C	D	E	F	G	H	I	J
Tb	21.8	23.8	23.2	23.3	23.5	22.8	23.1	22.9	23.0	24.2
Wear resistance	119	134	130	130	141	128	130	129	128	140
Blending method	in situ ①									
	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
Polymer	A	B	C	D	E	F	G	H	I	J
Tb	24.1	26.0	25.7	25.8	25.8	24.9	25.7	25.0	24.9	26.5
Wear resistance	183	221	210	208	237	204	207	201	202	230
Blending method	in situ ②									
	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27	Example 28	Example 29	Example 30
Polymer	A	B	C	D	E	F	G	H	I	J
Tb	23.9	25.9	25.4	25.7	25.8	24.6	25.3	25.1	24.8	26.4
Wear resistance	167	186	183	181	197	180	181	179	180	191

Inorganic compound	Alumina hydrate (boehmite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 11	Comparative Example 12	Comparative Example 13	Comparative Example 14	Comparative Example 15	Example 31	Example 32	Example 33	Example 34	Example 35
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	22.1	23.1	23.0	22.9	23.4	24.0	25.3	25.4	25.3	25.7
Wear resistance	100	109	108	112	107	108	121	119	125	118

Table 7

Compounding recipe A

Inorganic compound	γ-alumina									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 16	Comparative Example 17	Comparative Example 18	Comparative Example 19	Comparative Example 20	Example 36	Example 37	Example 38	Example 39	Example 40
APolymer	A	B	C	E	G	A	B	C	E	G
Tb	21.2	22.4	22.6	22.1	22.5	23.4	24.6	24.6	24.7	24.5
Wear resistance	100	107	107	110	108	110	118	116	122	120

Inorganic compound	Calcined clay									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 21	Comparative Example 22	Comparative Example 23	Comparative Example 24	Comparative Example 25	Example 41	Example 42	Example 43	Example 44	Example 45
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	21.5	22.6	22.3	22.3	22.4	23.3	24.7	24.5	24.7	24.5
Wear resistance	100	107	106	111	108	109	118	117	120	116

Inorganic compound	Kaolin									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 26	Comparative Example 27	Comparative Example 28	Comparative Example 29	Comparative Example 30	Example 46	Example 47	Example 48	Example 49	Example 50
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	21.5	22.6	22.3	22.3	22.4	23.3	24.7	24.5	24.7	24.5
Wear resistance	100	107	106	111	108	109	118	117	120	116

Inorganic compound	Magnesium hydroxide									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 31	Comparative Example 32	Comparative Example 33	Comparative Example 34	Comparative Example 35	Example 51	Example 52	Example 53	Example 54	Example 55
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	20.9	22.6	22.4	22.2	22.5	21.9	23.8	23.5	23.7	23.8
Wear resistance	100	116	114	120	115	122	143	140	145	138

Inorganic compound	Titanium oxide (anatase)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 36	Comparative Example 37	Comparative Example 38	Comparative Example 39	Comparative Example 40	Example 56	Example 57	Example 58	Example 59	Example 60
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	22.5	23.4	23.4	23.5	24.1	23.2	24.5	24.3	24.3	24.4
Wear resistance	100	107	108	111	106	108	122	120	125	120

Table 8

Compounding recipe B

Inorganic compound	Aluminum hydroxide (gibbsite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 41	Comparative Example 42	Comparative Example 43	Comparative Example 44	Comparative Example 45	Example 61	Example 62	Example 63	Example 64	Example 65
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	22.1	23.8	23.6	23.4	23.3	23.2	24.9	25.1	24.5	24.8
Wear resistance	100	115	113	118	113	112	129	126	134	125
Blending method	in situ ①					in situ ②				
	Example 66	Example 67	Example 68	Example 69	Example 70	Example 71	Example 72	Example 73	Example 74	Example 75
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	25.9	26.8	27.0	26.7	26.8	25.4	26.7	26.5	26.4	26.6
Wear resistance	143	170	165	174	166	140	164	162	171	161

Inorganic compound	Alumina hydrate (boehmite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 46	Comparative Example 47	Comparative Example 48	Comparative Example 49	Comparative Example 50	Example 76	Example 77	Example 78	Example 79	Example 80
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	24.1	25.2	24.9	25.0	24.9	26.1	27.3	27.0	26.9	27.0
Wear resistance	100	109	110	114	109	107	125	122	127	123

Inorganic compound	γ-alumina									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 51	Comparative Example 52	Comparative Example 53	Comparative Example 54	Comparative Example 55	Example 81	Example 82	Example 83	Example 84	Example 85
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	23.5	24.7	24.6	24.4	24.5	24.9	26.3	26.0	26.1	25.9
Wear resistance	100	108	107	111	107	107	121	120	123	119

Inorganic compound	Calcined clay									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 56	Comparative Example 57	Comparative Example 58	Comparative Example 59	Comparative Example 60	Example 86	Example 87	Example 88	Example 89	Example 90
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	23.9	25.0	24.9	24.9	25.3	25.1	26.3	26.0	25.9	26.2
Wear resistance	100	109	108	113	109	108	123	120	126	121

Table 9

Compounding recipe B

Inorganic compound	Kaolin									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 61	Comparative Example 62	Comparative Example 63	Comparative Example 64	Comparative Example 65	Example 91	Example 92	Example 93	Example 94	Example 95
APolymer	K	L	M	N	O	K	L	M	N	O
Tb	23.3	24.2	24.5	24.1	24.4	25.6	26.7	26.6	26.4	26.1
Wear resistance	100	110	109	114	110	111	124	122	129	123

Inorganic compound	Magnesium hydroxide									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 66	Comparative Example 67	Comparative Example 68	Comparative Example 69	Comparative Example 70	Example 96	Example 97	Example 98	Example 99	Example 100
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	23.2	24.2	24.2	24.1	23.8	24.4	25.5	25.2	25.2	25.4
Wear resistance	100	120	119	126	118	120	144	139	149	137

Inorganic compound	Titanium oxide (anatase)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 71	Comparative Example 72	Comparative Example 73	Comparative Example 74	Comparative Example 75	Example 101	Fxample 102	Example 103	Example 104	Example 105
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	24.2	25.3	25.1	25.3	24.9	25.2	26.4	26.3	26.1	26.1
Wear resistance	101	108	107	112	107	110	123	119	127	121

Table 10

Compounding recipe C

Inorganic compound	Aluminum hydroxide (gibbsite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 76	Comparative Example 77	Comparative Example 78	Comparative Example 79	Comparative Example 80	Example 106	Example 107	Example 108	Example 109	Example 110
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	9.1	12.0	12.1	11.8	11.7	13.4	16.1	15.8	15.7	15.9
Wear resistance	100	153	149	184	144	169	231	225	267	228
Blending method	in situ ①					in situ ②				
	Example 111	Example 112	Example 113	Example 114	Example 115	Example 116	Example 117	Example 118	Example 119	Example 120
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	22.0	24.1	23.8	23.7	23.5	20.4	22.7	23.0	22.5	22.6
Wear resistance	331	407	398	433	402	312	394	386	420	387

Inorganic compound	Alumina hydrate (boehmite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 81	Comparative Example 82	Comparative Example 83	Comparative Example 84	Comparative Example 85	Example 121	Example 122	Example 123	Example 124	Example 125
Polymer	K	L	M	N	O	K	L	M	N	O
Tb	11.9	14.1	14.3	13.7	14.0	18.4	20.5	20.7	19.9	20.3
Wear resistance	100	140	139	149	137	143	174	172	189	165

Table 11

Compounding recipe D

Inorganic compound	Aluminum hydroxide (gibbsite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 86	Comparative Example 87	Comparative Example 88	Comparative Example 89	Comparative Example 90	Example 126	Example 127	Example 128	Example 129	Example 130
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	21.7	23.0	22.9	22.5	23.1	23.6	24.8	24.9	24.5	24.5
Wear resistance	100	118	115	124	114	112	133	131	140	129
Blending method	in situ ①					in situ ②				
	Example 131	Example 132	Example 133	Example 134	Example 135	Example 136	Example 137	Example 138	Example 139	Example 140
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	25.6	26.4	26.4	26.2	26.6	25.5	26.5	26.2	26.4	26.5
Wear resistance	151	176	171	182	173	137	168	165	177	168

Inorganic compound	Alumina hydrate (boehmine)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 91	Comparative Example 92	Comparative Example 93	Comparative Example 94	Comparative Example 95	Example 141	Example 142	Example 143	Example 144	Example 145
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	24.1	25.1	25.2	24.9	25.1	25.2	26.0	26.0	25.9	26.3
Wear resistance	100	115	112	120	113	111	129	130	136	128

Inorganic compound	γ-alumina									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 96	Comparative Example 97	Comparative Example 98	Comparative Example 99	Comparative Example 100	Example 146	Example 147	Example 148	Example 149	Example 150
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	22.8	23.9	24.1	23.8	24.0	25.1	26.0	25.8	26.3	25.9
Wear resistance	100	114	110	116	111	114	132	130	137	130

Inorganic compound	Calcined clay									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 101	Comparative Example 102	Comparative Example 103	Comparative Example 104	Comparative Example 105	Example 151	Example 152	Example 153	Example 154	Example 155
Polymer	A	B	C	E	G	A	B	C	E	G
Tb	22.7	24.2	24.0	23.8	24.0	24.7	26.1	25.9	25.7	25.8
Wear resistance	100	112	110	116	113	105	126	123	133	127

Table 12

Compounding recipe E

Inorganic compound	Aluminum hydroxide (gibbsite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 106	Comparative Example 107	Comparative Example 108	Comparative Example 109	Comparative Example 110	Example 156	Example 157	Example 158	Example 159	Example 160
Polymer	P	Q	R	S	T	P	Q	R	S	T
Tb	18.6	20.2	19.9	19.7	20.0	19.7	21.3	21.0	21.3	21.5
Wear resistance	100	111	110	114	110	108	122	119	125	118
Blending method	in situ ①					in situ ②				
	Example 161	Example 162	Example 163	Example 164	Example 165	Example 166	Example 167	Example 168	Example 169	Example 170
Polymer	P	Q	R	S	T	P	Q	R	S	T
Tb	22.7	24.9	24.5	24.4	24.6	22.3	24.4	24.5	24.6	24.2
Wear resistance	131	153	149	156	147	128	147	145	150	144

Inorganic compound	Alumina hydrate (boehmite)									
Blending method	DRY					Aqueous dispersion				
	Comparative Example 111	Comparative Example 112	Comparative Example 113	Comparative Example 114	Comparative Example 115	Example 171	Example 172	Example 173	Example 174	Example 175
Polymer	P	Q	R	S	T	P	Q	R	S	T
Tb	20.4	21.5	21.5	21.1	21.4	21.8	23.3	23.4	23.2	23.0
Wear resistance	100	107	108	110	107	105	118	116	120	117

Table 13

Inorganic compound	Gibbsite				Boehmite		γ-alumina		Calcined clay		Kaolin		Magnesium hydroxide		Anatase	
	DRY	aqueous dispersion	in situ ①	in situ ②	DRY	aqueous dispersion	DRY	aqueous dispersion	DRY	aqueous dispersion	DRY	aqueous dispersion	DRY	aqueous dispersion	DRY	aqueous dispersion
Compounding recipe A Polymer A																
Tb	20.1	21.8	24.1	23.9	22.1	24.0	21.2	23.4	21.5	23.3	21.4	23.9	20.9	21.9	22.5	23.2
Wear resistance	100	119	183	167	100	108	100	110	100	109	100	116	100	122	100	108
Compounding recipe B Polymer K																
Tb	22.1	23.2	25.9	25.4	24.1	26.1	23.5	24.9	23.9	25.1	23.3	25.6	23.2	24.4	24.2	25.2
Wear resistance	100	112	143	140	100	107	100	107	100	108	100	111	100	120	100	110
Compounding recipe C Polymer K																
Tb	9.1	13.4	22.0	20.4	11.9	18.4										
Wear resistance	100	169	331	312	100	143										
Compounding recipe D Polymer A																
Tb	21.7	23.6	25.6	25.5	24.1	25.2	22.8	25.1	22.7	24.7						
Wear resistance	100	112	151	137	100	111	100	114	100	105						
Compounding recipe E Polymer P																
Tb	18.6	19.7	22.7	22.3	20.4	21.8										
Wear resistance	100	108	131	128	100	105										

[0105] As shown in Tables 6-13, all examples are large in Tb value (tensile strength) and wear resistance as compared with the corresponding comparative examples and excellent in any performances. Particularly, in case of in-Situ ① and②, the value of Tb and wear resistance become larger, and it has been confirmed that any performances are very excellent. And also, it is particularly seen from Table 13 that the tensile strength and wear resistance are considerably improved in gibbsite (aluminum hydroxide) and kaolin among the given inorganic compounds as compared with dry-type milling (Comparative Examples). Moreover, it has been found that boehmite and calcined clay are very excellent in the effect of improving the Tb value, and magnesium hydroxide is very excellent in the wear resistance.

[0106] As mentioned above, in the vulcanized rubbers made of the rubber compositions each containing the composite according to the invention, the tensile strength and wear resistance are very excellent and the dispersibility of the inorganic compound into the diene-based rubber composition and the vulcanized rubber is very good.

[0107] Then, an embodiment using colloidal silica or alumina sol as an inorganic compound in the composite material will be described.

(1) Production of SBR latex

[0108] As SBR latex used in the following examples and comparative examples, synthesis is carried out based on a cold recipe of E-SBR polymerization recipe examples in Table 10.1, page 300 of "Production Process of New Polymers" published by Kogyo Chosakai (edited by Yasuharu Saeki and Shinzo Omi). Moreover, monomers for SBR (BR) are charged at a ratio shown in Table 14 and reaction thereof is progressed at a polymerization temperature of 5°C. At a time that conversion reaches 60%, N,N-dimethyl dithiocarbamate is added to stop polymerization. Thereafter, SBR (BR) latex is obtained by recovering unreacted monomers through an evaporator.

(2) Production of rubbery polymer

[0109] A part of the latex obtained in the above item (1) is sampled and coagulated with sulfuric acid and salt to form a crumb, and a solid matter is dried to obtain a rubbery copolymer. The microstructure and Mooney viscosity are measured with respect to this copolymer. The results are shown in Table 14.

Table 14

Copolymer latex		A	B	C
Feed amount (part by mass)	butadiene	71	59	100
	styrene	29	41	0
Bonding content (wt %)	styrene content	24.0	35.5	0.0
Mooney viscosity (ML_{1+4}, 100°C)		49	51	50
Concentration of copolymer (%)		20	20	20

(3) Production of master batch

[0110] The SBR (BR) latex obtained in the above item (2) is blended with colloidal silica or alumina sol shown in Table 15 at a blending ratio shown in Table 16, stirred with a mechanical stirrer for 30 minutes, and neutralized with a diluted sulfuric acid. Then, a master batch is obtained by drying through a drum drier having a surface temperature of 130°C to remove water.

Table 15

Commercially available grade name	Manufacturer	Particle size (mm)	Specific surface area (m^2/g)	SiO_2 (%)	Al_2O_3 (%)	pH
Snowtex 30	Nissan Chemical Industries, Ltd.	15	200	30.4	-	9.9
Snowtex C	Nissan Chemical Industries, Ltd.	15	200	20.4	-	8.8
Snowtex O	Nissan Chemical Industries, Ltd.	15	200	20.5	-	2.9

Table 15 (continued)

Commercially available grade name	Manufacturer	Particle size (mm)	Specific surface area (m^2/g)	SiO_2 (%)	Al_2O_3 (%)	pH
Snowtex S	Nissan Chemical Industries, Ltd.	10	300	30.5	-	9.8
Snowtex XS	Nissan Chemical Industries, Ltd.	5	560	20.3	-	9.2
Snowtex UP	Nissan Chemical Industries, Ltd.	20 (chain)	150	20.3	-	10.4
LUDOX HS-30	DuPont	12	220	30.0	-	9.8
LUDOX SM-30	DuPont	8	345	30.0	-	10.0
LUDOX TM-40	DuPont	19	140	40.0	-	9.0
Alumina sol-200	Nissan Chemical Industries, Ltd.	100×10	300	-	10.8	4.7
Alumina sol-520	Nissan Chemical Industries, Ltd.	15	200	-	20.5	4.0

Table 16

Master batch sample	Colloidal solution used, amount (g)	Latex, amount (g)	SiO_2 (phr)	Al_2O_3 (phr)
a	Snowtex 30 164.5	A 500	50	-
b	Snowtex C 245.1	A 500	50	-
c	Snowtex O 243.9	A 500	50	-
d	Snowtex S 163.9	A 500	50	-
e	Snowtex XS 2 46.3	A 500	50	-
f	Snowtex UP 246.3	A 500	50	-
g	LUDOX HS-30 166.7	A 500	50	-
h	LUDOX SM-30 166.7	A 500	50	-
i	LUDOX TM-40 125.0	A 500	50	-
j	Alumina sol-200 463.0	A 500	-	50
k	Alumina sol-520 243.9	A 500	-	50
l	Snowtex 30 164.5	B 500	50	-
m	Snowtex 30 164.5	C 500	50	-
n	Snowtex S 163.9	B 500	50	-
o	Snowtex S 163.9	C 500	50	-
p	Snowtex 30 82.2	A 500	25	-
q	Snowtex S 82.0	A 500	25	-

Examples 176-198 and Comparative Examples 116-132

[0111] Rubber compositions are prepared according to compounding recipes shown in Table 17 by using master batches a-q obtained in the above item (3) with respect to examples and rubbery polymers A-C obtained in the above item (2) with respect to comparative examples. With respect to the resulting rubber compositions, a Mooney viscosity (comp $ML_{1+4}(100°C)$) is measured, while tensile properties, low heat build-up property and rebound resilience are measured with respect to vulcanized rubbers to obtain results as shown in Table 18.

Table 17-1

			Compounding recipe 1
Stage	first milling	master batch SBR prepared	150(100)
		carbon black	0
		silica	0(50)
		aromatic oil	10
		stearic acid	2
		silane coupling agent Si69	5
		6C	1
Stage	final	ZnO	3
		DPG	1
		DM	1
		NS	1
		sulfur	1.5

Table 17-2

			Compounding recipe 2	Compounding recipe 3	Compounding recipe 4
Stage	first milling	master batch SBR prepared	125(100)	125(100)	100(80)
		NR	0	0	20
		carbon black	25	25	25
		silica	0(25)	0(25)	5(25)
		silane coupling agent Si69	0	2.5	2.5
		aromatic oil	10	10	10
		stearic acid	2	2	2
		6C	1	1	1
Stage	final	ZnO	3	3	3
		DPG	0.8	0.8	0.8
		DM	1	1	1
		NS	1	1	1
		sulfur	2.5	1.5	1.5

Table 18-1

Evaluation No. of properties	1	2	3	4	5	6	7	8	9	10	11	12
	Comparative Example 116	Comparative Example 117	Comparative Example 118	Comparative Example 119	Example 176	Example 177	Example 178	Example 179	Example 180	Example 181	Example 182	Example 183
Master batch SBR (BR)					a	b	c	d	e	f	g	h
Copolymer	A	A	B	B								
Kind of silica	AQ	AQ	KQ	KQ								
Milling stage	2	3	2	3	2	2	2	2	2	2	2	2
Fracture properties Tb	17.5	19.0	25.7	28.0	24.3	26.6	27.3	29.0	30.3	26.5	26.0	29.2
M_{300}	13.3	13.9	13.7	14.3	16.1	15.5	15.5	17.7	18.4	13.8	17.2	16.9
Low heat build-up property Tan σ	0.143	0.137	0.136	0.131	0.122	0.133	0.121	0.123	0.119	0.122	0.136	0.122
Rebound resilience (%)	45	47	41	43	49	48	49	45	43	48	48	45
comp ML1+4 (100°C)	72.0	61.1	120.9	97.5	65.7	70.3	68.7	78.3	82.4	62.8	67.0	72.1

Evaluation No. of properties	13	14	15	16	17	18	19	20	21	22	23	24
	Example 184	Comparative Example 120	Comparative Example 121	Comparative Example 122	Comparative Example 123	Example 185	Example 186	Example 187	Example 188	Comparative Example 124	Example 189	Example 190
Master batch SBR (BR)	i					l	m	n	o		j	k
Copolymer		B	C	B	C					A		
Kind of silica		AQ	AQ	KQ	KQ					aluminum hydroxide powder		
Milling stage	2	2	2	2	2	2	2	2	2	2	2	2
Fracture properties Tb	22.5	19.6	16.3	26.6	23.5	26.0	23.4	30.7	27.6	5.3	8.5	20.6
M_{300}	13.2	13.7	12.8	14.1	13.1	16.4	15.5	18.0	17.3	4.2	5.3	9.0
Low heat build-up property Tan σ	0.129	0.149	0.129	0.141	0.124	0.128	0.107	0.130	0.111	0.086	0.099	0.169
Rebound resilience (%)	53	43	49	39	45	47	51	43	46	65	62	59
comp ML1+4 (100°C)	54.1	71.1	73.3	118.5	122.6	64.4	67.2	76.0	79.7	31.1	52.9	45.5

Nipsil AQ, made by Nippon Silica Industrial Co., Ltd.
Nipsil KQ, made by Nippon Silica Industrial Co., Ltd.

Table 18-2

Evaluation No. of properties	25	16	27	28	29	30	31	32
	Comparative Example 125	Comparative Example 126	Example 191	Example 192	Comparative Example 127	Comparative Example 128	Example 193	Example 194
Master batch SBR (BR)			a	d			a	d
Copolymer	A	A			A	A		
Kind of silica	AQ	KQ			AQ	KQ		
Fracture properties Tb	18.5	26.2	25.8	30.1	19.3	27.4	26.9	30.8
M_{300}	13.8	14.1	16.2	18.0	14.2	14.5	16.4	18.3
Low heat build-up property Tan σ	0.147	0.139	0.126	0.130	0.151	0.145	0.129	0.133
Rebound resilience (%)	40	37	45	40	42	38	46	41
comp ML1+4 (100°C)	85.3	113.6	68.7	79.0	66.5	91.3	62.1	73.8

Evaluation No. of properties	33	34	35	36	37	38	39	40
	Comparative Example 129	Comparative Example 130	Example 195	Example 196	Comparative Example 131	Comparative Example 132	Example 197	Example 198
Master batch SBR (BR)			a	d			m	o
Copolymer	A	A			C	C		
Kind of silica	AQ	KQ			AQ	KQ		
Fracture properties Tb	20.2	27.8	27.3	31.0	18.5	25.2	25.0	29.3
M_{300}	14.6	14.8	16.6	18.5	13.7	14.0	16.3	18.1
Low heat build-up property Tan σ	0.144	0.140	0.120	0.125	0.130	0.123	0.108	0.114
Rebound resilience (%)	44	40	48	43	48	45	50	47
comp ML1+4 (100°C)	70.9	96.4	66.8	78.7	71.5	98.4	65.3	78.0

Nipsil AQ, made by Nippon Silica Industrial Co., Ltd.
Nipsil KQ, made by Nippon Silica Industrial Co., Ltd.

[0112] According to the invention, the dispersibility of the inorganic compound into the diene-based rubber can be considerably improved by using a master batch obtained by mixing an aqueous dispersion of a diene-based rubber with an aqueous dispersion of an inorganic compound. Particularly, when silica is used as the inorganic compound, the Mooney viscosity can be largely reduced while maintaining good tensile properties, low heat-build-up property and rebound resilience. Therefore, the milling number and milling time of rubber-silica mixture can be decreased, whereby the effect of improving the productivity can be obtained.

[0113] Next, an embodiment using fine particles of aluminum hydroxide having a gibbsite structure as an inorganic compound below:

[0114] The diene-based rubbers (oil extension and non-oil extension) used in the following examples and comparative examples are shown in Table 19. They correspond to Tables 1 and 2.

Table 19

	St (%)	Third monomer	Oil extending amount (phr)
Polymer A	35	-	37.5
Polymer B	35	hydroxyethyl methacrylate	37.5
Polymer C	35	diethylaminoethyl methacrylate	37.5
Polymer E	35	acrylonitrile	37.5
Polymer G	35	itaconic acid	37.5
Polymer K	23.5	-	0
Polymer L	23.5	hydroxyethyl methacrylate	0
Polymer N	23.5	acrylonitrile	0

[0115] As the inorganic compound, aluminum hydroxide (Higilite H-43M, made by Showa Denko Co., Ltd. particle size: 0.72 μm, BET surface area: 6.4 m^2/g) is pulverized by using a planetary ball mill to obtain fine particles having a particle size: 0.38 μm and a BET surface area: 12.1 m^2/g. 40 g of the fine particles are added with 160 g of distilled water in a colloid mill to form a slurry. And also, the fine particles are directly milled in the compounding without forming the slurry in the comparative examples.

[0116] Moreover, the particle size is determined by the following method for the measurement through a centrifugal settlement analysis. Measuring apparatus: super-fine particle size analytical meter through highspeed disc centrifugal process (name of measuring apparatus: BI-DIP, made by BROOKHAVEN INSTRUMENTS CORPORATION)
Measuring method: A sample is added with a small amount of a surfactant and mixed with an aqueous solution of 20 volume% ethanol to form a dispersion having a sample concentration of 200 mg/l, which is sufficiently dispersed in a super-sonic homogenizer to obtain a specimen. After a revolution number of the apparatus is set to 8,000 rpm and a spinning solution (pure water, 24°C) is added, 0.5 ml of a specimen dispersion is poured to start measurement. A weight average diameter (Dw) of a coagulate calculated by a photoelectric settlement method is rendered into a value of particle size. Examples 199-209, Comparative Examples 133-143

[0117] Rubber compositions are prepared according to compounding recipes A, B, D shown in Table 20 by using the polymer shown in Table 19, and the aforementioned slurry of fine particles of aluminum hydroxide having the gibbsite structure with respect to the examples or by compounding aluminum hydroxide (Higilite H-43M) or its finely pulverized product as it is with respect to the comparative examples, and then the tensile strength and wear resistance are measured to obtain results shown in Tables 21 to 23. Moreover, the wear resistance is represented by an index on the basis that Comparative Examples 1, 41 and 86 are used as a control, respectively.

[0118] As seen from Tables 21 to 23, when aluminum hydroxide having the gibbsite structure is finely pulverized, the reinforcing property is improved, and further when the aqueous dispersion is used to form the composite, the dispersibility is improved, and hence the tensile strength and wear resistance are considerably improved as compared with those of the respective comparative example.

Table 20

Unit: part by mass				
Milling stage	Compounding recipe	A	B	D
1st	oil-extended SBR	137.5		137.5
	non-oil extended SBR		100	
	N339 (Seast KH)	60	40	30
	Nipsil AQ			30
	aluminum hydroxide	30	20	30
	aromatic oil		10	
	stearic acid	2	2	2
	6C	1	1	1
	Si69			3
2nd	ZnO	3	3	3
	DPG	0.8	0.8	0.8
	DM	1	1	1
	NS	1	1	1
	sulfur	1.5	1.5	1.5

Table 21

Compounding recipe A					
Inorganic filler	Aluminum hydroxide (gibbsite) (fine particle size)				
Blending method	DRY				
	Comparative Example 133	Comparative Example 134	Comparative Example 135	Comparative Example 136	Comparative Example 137
Polymer	A	B	C	E	G
Tb	21.5	22.9	22.4	22.5	22.3
Wear resistance	113	124	120	127	119
Blending method	Aqueous dispersion				
	Example 199	Example 200	Example 201	Example 202	Example 203
Polymer	A	B	C	E	G
Tb	24.0	25.1	24.6	24.9	24.5
Wear resistance	130	145	138	148	137

Table 22

Compounding recipe B						
Inorganic filler	Aluminum hydroxide (gibbsite) (fine particle size)					
Blending method	DRY			Aqueous dispersion		
	Comparative Example 138	Comparative Example 139	Comparative Example 140	Example 204	Example 205	Example 206
Polymer	K	L	N	K	L	N
Tb	23.0	24.8	24.3	25.1	26.8	26.5
Wear resistance	109	125	120	130	141	144

Table 23

Compounding recipe D						
Inorganic filler	Aluminum hydroxide (gibbsite) (fine particle size)					
Blending method	DRY			Aqueous dispersion		
	Comparative Example 141	Comparative Example 142	Comparative Example 143	Example 207	Example 208	Example 209
Polymer	A	B	E	A	B	E
Tb	22.9	24.5	24.1	25.0	26.5	26.3
Wear resistance	108	112	133	131	146	150

INDUSTRIAL APPLICABILITY

[0119] In the diene-based rubber-inorganic compound composite material and/or rubber composition according to the invention, the dispersibility of the inorganic compound into the diene-based rubber is very excellent, so that there can be provided a vulcanized rubber (rubber article) having very excellent rubber properties such as wear resistance, tensile strength and the like. Particularly, when using an aqueous solution of an inorganic salt or a solution of an organometallic compound capable of forming the inorganic compound of the formula (I), the dispersibility is more excellent, and hence there can be provided a rubber composition having very excellent rubber properties such as wear resistance, tensile strength and the like.

Claims

1. A diene-based rubber-inorganic compound composite material comprising a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10), and produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous dispersion of the inorganic compound.

2. A diene-based rubber-inorganic compound composite material according to claim 1, wherein the aqueous solution of the inorganic compound is prepared by adding an acid or an alkali to an aqueous solution of an inorganic salt capable of forming the compound of the formula (I).

3. A diene-based rubber-inorganic compound composite material according to claim 2, wherein the inorganic salt is at least one selected from metal salts and oxo acid salts of metals.

4. A diene-based rubber-inorganic compound composite material according to claim 3, wherein the metal constituting the metal salt or oxo acid salt of metal is aluminum.

5. A diene-based rubber-inorganic compound composite material according to claim 1, wherein the aqueous solution of the inorganic compound is prepared by adding water, an acid or an alkali to a solution of an organometallic compound capable of forming the compound of the formula (I).

6. A diene-based rubber-inorganic compound composite material according to claim 1, wherein the aqueous solution of the inorganic compound is prepared by adding an alkali to a metal shown in the formula (I).

7. A diene-based rubber-inorganic compound composite material comprising a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad \text{(I)}$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10), and produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous solution of an inorganic salt capable of forming the inorganic compound represented by the formula (I).

8. A diene-based rubber-inorganic compound composite material according to claim 7, wherein the inorganic salt is at least one of metal salts and oxo acid salts of metals.

9. A diene-based rubber-inorganic compound composite material according to claim 8, wherein the metal constituting the metal salt or the oxo acid salt of the metal is aluminum.

10. A diene-based rubber-inorganic compound composite material comprising a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad \text{(I)}$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10), and produced through a step of mixing an aqueous dispersion of the diene-based rubber with a solution of an organometallic compound capable of forming the inorganic compound represented by the formula (I).

11. A diene-based rubber-inorganic compound composite material according to any one of claims 1 to 10, wherein a diene-based rubber latex synthesized by an emulsion polymerization is used as the aqueous solution of the diene-based rubber.

12. A diene-based rubber-inorganic compound according to any one of claims 1 to 10, wherein the diene-based rubber is a diene-based rubber containing a polar group with a heteroatom.

13. A diene-based rubber-inorganic compound composite material according to claim 12, wherein the polar group is a hydroxyl group, an oxy group, an alkoxysilyl group, an epoxy group, a carboxyl group, a carbonyl group, an oxycarbonyl group, a sulfide group, a disulfide group, a sulfonyl group, a sulfinyl group, a thiocarbonyl group, an imino group, an amino group, a nitrile group, an ammonium group, an imido group, an amido group, a hydrazo group, an azo group or a diazo group.

14. A diene-based rubber-inorganic compound composite material according to any one of claims 1 to 13, wherein the compound of the formula (I) is a compound represented by the following formula (II):

$$Al_2O_3 \cdot mSiO_2 \cdot nH_2O \qquad (II)$$

(wherein m is a number of 0-4 and n is a number of 0-4).

15. A method of producing a diene-based rubber-inorganic compound composite material which comprises mixing an aqueous dispersion of a diene-based rubber with an aqueous dispersion of an inorganic compound.

16. A method of producing a diene-based rubber-inorganic compound composite material according to claim 15, wherein a solvent of the aqueous dispersion is water.

17. A method of producing a diene-based rubber-inorganic compound composite material according to claim 15, wherein the aqueous dispersion of the inorganic compound has a pH of 8.5-11.

18. A method of producing a diene-based rubber-inorganic compound composite material according to claim 15, wherein the aqueous dispersion of the inorganic compound has a pH of 2-4.

19. A method of producing a diene-based rubber-inorganic compound composite material which comprises a step of mixing an aqueous dispersion of a diene-based rubber with an aqueous dispersion of at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10).

20. A method of producing a diene-based rubber-inorganic compound composite material according to claim 19, wherein the aqueous solution of the inorganic compound is prepared by adding an acid or an alkali to an aqueous solution of an inorganic salt capable of forming the compound of the formula (I).

21. A method of producing a diene-based rubber-inorganic compound composite material according to claim 20, wherein the inorganic salt is at least one selected from metal salts and oxo acid salts of metals.

22. A method of producing a diene-based rubber-inorganic compound composite material according to claim 21, wherein the metal constituting the metal salt or oxo acid salt of metal is aluminum.

23. A method of producing a diene-based rubber-inorganic compound composite material according to claim 19, wherein the aqueous solution of the inorganic compound is prepared by adding water or an acid or an alkali to an aqueous solution of an organic metal compound capable of forming the compound of the formula (I):

24. A method of producing a diene-based rubber-inorganic compound composite material according to claim 19, wherein the aqueous solution of the inorganic compound is prepared by adding an alkali to the metal shown in the formula (I).

25. A method of producing a diene-based rubber-inorganic compound composite material which comprises a step of mixing an aqueous dispersion of a diene-based rubber with an aqueous solution of an inorganic salt capable of forming a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide or a metal

hydroxide, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10).

26. A method of producing a diene-based rubber-inorganic compound composite material according to claim 25, wherein the inorganic salt is at least one selected from metal salts and oxo acid salts of metals.

27. A method of producing a diene-based rubber-inorganic compound composite material according to claim 26, wherein the metal constituting the metal salt or oxo acid salt of metal is aluminum.

28. A method of producing a diene-based rubber-inorganic compound composite material which comprises a step of mixing an aqueous dispersion of a diene-based rubber with a solution of an organic metal compound capable of forming a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10).

29. A method of producing a diene-based rubber-inorganic compound composite material according to any one of claims 19 to 28, wherein a diene-based rubber latex synthesized by an emulsion polymerization is used as the aqueous solution of the diene-based rubber.

30. A method of producing a diene-based rubber-inorganic compound composite material according to any one of claims 19 to 29, which further comprises a step of co-coagulating the diene-based rubber and the inorganic compound with an electrolyte containing a metal salt and filtering and drying.

31. A method of producing a diene-based rubber-inorganic compound composite material according to any one of claims 19 to 30, wherein the diene-based rubber is a diene-based rubber containing a polar group with a heteroatom.

32. A method of producing a diene-based rubber-inorganic compound composite material according to claim 31, wherein the polar group is a hydroxyl group, an oxy group, an alkoxysilyl group, an epoxy group, a carboxyl group, a carbonyl group, an oxycarbonyl group, a sulfide group, a disulfide group, a sulfonyl group, a sulfinyl group, a thiocarbonyl group, an imino group, an amino group, a nitrile group, an ammonium group, an imido group, an amido group, a hydrazo group, an azo group or a diazo group.

33. A method of producing a diene-based rubber-inorganic compound composite material according to any one of claims 15 to 28, wherein the compound of the formula (I) is a compound represented by the following formula (II):

$$Al_2O_3 \cdot mSiO_2 \cdot nH_2O \qquad (II)$$

(wherein m is a number of 0-4 and n is a number of 0-4).

34. A rubber composition comprising a diene-based rubber-inorganic compound composite material, which comprises a diene-based rubber and at least one inorganic compound selected from silica and a compound represented by the following formula (I):

$$wM \cdot xSiO_y \cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10) and is produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous dispersion of the inorganic compound, and a crosslinking agent.

35. A rubber composition according to claim 34, wherein the aqueous solution of the inorganic compound is prepared by adding an acid or an alkali to an aqueous solution of an inorganic salt capable of forming the compound of the formula (I).

36. A rubber composition according to claim 35, wherein the inorganic salt is at least one selected from metal salts and oxo acid salts of metals.

37. A rubber composition according to claim 36, wherein the metal constituting the metal salt or oxo acid salt of metal is aluminum.

38. A rubber composition according to claim 34, wherein the aqueous solution of the inorganic compound is prepared by adding water, an acid or an alkali to a solution of an organometallic compound capable of forming the compound of the formula (I).

39. A rubber composition according to claim 34, wherein the aqueous solution of the inorganic compound is prepared by adding an alkali to a metal shown in the formula (I).

40. A rubber composition comprising a diene-based rubber-inorganic compound composite material, which comprises a diene-based rubber and an inorganic compound represented by the following formula (I):

$$wM\cdot xSiO_y\cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10) and is produced through a step of mixing an aqueous dispersion of the diene-based rubber with an aqueous solution of an inorganic salt capable of forming the inorganic compound represented by the formula (I), and a crosslinking agent.

41. A rubber composition according to claim 40, wherein the inorganic salt is at least one selected from metal salts and oxo acid salts of metals.

42. A rubber composition according to claim 41, wherein the metal constituting the metal salt or oxo acid salt of metal is aluminum.

43. A rubber composition comprising a diene-based rubber-inorganic compound composite material, which comprises a diene-based rubber and an inorganic compound represented by the following formula (I):

$$wM\cdot xSiO_y\cdot zH_2O \qquad (I)$$

(wherein M is at least one metal selected from the group consisting of Al, Mg, Ti and Ca or a metal oxide thereof or a metal hydroxide thereof, and w is a number of 1-5, x is a number of 0-10, y is a number of 2-5 and z is a number of 0-10) and is produced through a step of mixing an aqueous dispersion of the diene-based rubber with a solution of an organic metal compound capable of forming the inorganic compound represented by the formula (I), and a crosslinking agent.

44. A rubber composition according to any one of claims 34 to 43, wherein a diene-based rubber latex synthesized by an emulsion polymerization is used as the aqueous solution of the diene-based rubber.

45. A rubber composition according to any one of claims 34 to 43, wherein the diene-based rubber is a diene-based rubber containing a polar group with a heteroatom.

46. A rubber composition according to claim 45, wherein the polar group is a hydroxyl group, an oxy group, an alkoxysilyl group, an epoxy group, a carboxyl group, a carbonyl group, an oxycarbonyl group, a sulfide group, a disulfide group, a sulfonyl group, a sulfinyl group, a thiocarbonyl group, an imino group, an amino group, a nitrile group, an ammonium group, an imido group, an amido group, a hydrazo group, an azo group or a diazo group.

47. A rubber composition according to any one of claims 34 to 46, wherein the compound of the formula (I) is a compound represented by the following formula (II):

$$Al_2O_3 \cdot mSiO_2 \cdot nH_2O \tag{I}$$

(wherein m is a number of 0-4 and n is a number of 0-4).

48. A rubber composition according to any one of claims 34 to 47, wherein the diene-based rubber-inorganic compound composite material is included in an amount of not less than 10 mass%, and the crosslinking agent is a vulcanizing agent, and further a reinforcing filler is contained.

49. A rubber composition according to claim 48, wherein the reinforcing filler contains at least one of carbon black and silica.

50. A rubber composition according to any one of claims 34 to 49, which further contains a silane coupling agent.

51. A rubber composition according to any one of claims 34 to 50, which further contains an aliphatic acid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/07743

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl⁷ C08L9/00, C08L7/00, C08L13/00, C08J3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl⁷ C08L9/00, C08L7/00, C08L13/00, C08J3/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent WPLI "C08L9/00","C08L7/00","C08J3/22","DISPERSION" in abstract

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 50-052145 A (Agency of Industrial Science and Technology), 09 May, 1975 (09.05.75), Claims; page 1, lower right column, lines 8 to 19 (Family: none)	1-51
A	JP 62-256835 A (Toyoda Gosei Co., Ltd.), 09 November, 1987 (09.11.87), Claims (Family: none)	1-51

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 October, 2001 (29.10.01)	06 November, 2001 (06.11.01)
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